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Classe des Sciences Mathématiques et Naturelles. — Série A : Sciences Mathématiques
1950

On the Quaternary Azeotrope *n*-Heptane-Benzen-Ethanol-Water. I

On the Quaternary Azeotrope Benzene-Ethanol-Water-Isooctane. II

On the Quaternary Azeotrope Composed of Benzene, Ethanol, Water and Cyclohexane. III

by

W. Świętosławski, and K. Zięborak

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1950

O azeotropie czteroskładnikowym n-heptan-benzen-etanol-woda. On the Quaternary Azeotrope n Heptane-Benzen-Ethanol-Water. I.

Note

de M. **W. ŚWIĘTOSŁAWSKI** et **K. ZIĘBORAK,**

présentée le 30 Mars 1950

No quaternary azeotropes have been found as yet in spite of the fact that in numerous distillations of polycomponent systems some of these azeotropes might have been accumulated in the fractions collected in course of the distillation.

It would be reasonable to expect that if two ternary azeotropes *A-B-C* and *A-B-C'* formed a quaternary one, the azeotropic depression with respect to the lower boiling ternary azeotrope would be rather small

When carefully examining the distillation curve in the process of dehydration of ethanol by a mixture of benzene and that fraction of gasoline which contains predominantly isomeric heptanes, we came to the conclusion that quaternary azeotropes formed by ethanol, water, benzene and each of the heptanes should be considered as most probable To prove this assumption we used normal heptane, the sample of which boiled at 98·60° C, (water used as primary ebulliometric standard), and the difference found between the boiling and the condensation temperature determined in a differential ebulliometer of standardized dimensions (1) was equal to 0·138°. The sample was characterized by the first degree of purity according to the ebulliometric test (2). Two corresponding ternary azeotropes were prepared by a careful rectification and the following boiling temperatures were found 64·86° C and 69·07° The differences between the boiling and condensation temperatures 0·005° and 0·015° respectivaly indicated that the contaminations present in the benzene and *n*-heptane had been removed by distillation In fact the first

azeotrope was characterized by the fifth and the second by the fourth degree of purity, according to the same scale.

The ebulliometric method of detection of a quaternary azeotrope has been described by one of us [3]. It consisted in filling a differential ebulliometer for purity test with the lower boiling ternary azeotrope and in adding successively small amounts of the higher boiling azeotrope. After each addition of a new quantity of this azeotrope one has to determine the boiling and the condensation temperatures and to plot them against the percentage of the mixture added. If for both of the curves first a decrease, then a minimum point, and finally a further decrease of both of the temperatures were noted, this would be a proof of the existence of a quaternary azeotrope. This method could be applied in our case with a small modification. In fact the higher boiling azeotrope was composed of two liquid phases for this reason it was necessary to add successively *n*-heptane and a mixture of water and ethanol prepared according to the composition of the azeotrope.

Side by side another differential ebulliometer filled with the lower boiling ternary azeotrope (benzene-ethanol-water) was placed and put in to action to serve as standard. For convenience two Roberteau thermometers were used and transferred from one ebulliometer into the other so that very small temperature changes could be measured. We actually found the expected minima of the boiling and condensation temperatures. Due to the small amount of impurities present in the *n*-heptane the minimum of the condensation temperature was slightly displaced toward the somewhat lower concentration of the azeotrope added. In figure 1 the two curves are shown. The azeotrope depression with respect to the azeotrope benzene-ethanol-water was found to be 0.070°, so that its normal boiling temperature is 64.79° C.

Independently the quaternary azeotrope was prepared by distillation. Practically the same boiling temperature within $\pm 0.004°$ was found for this sample. It was used for determining the composition. In table I details of the analysis are given. In column I the percentage of the two phase mixture is given, in columns II and III the weight percentages of components for the lower and for the upper phase are listed.

TABLE I

Component	I Weight %	II Weight %	III Weight %
Benzene	62·4	11·8	73·5
n-Heptane	12·1	0·9	14·5
Ethanol	18·7	54·4	11·0
Water	6·8	32·9	1·0
	100%	100%	100%

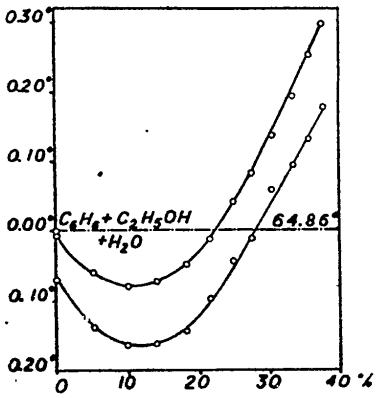

Fig. 1. Boiling and condensation temperatures of mixtures of azeotropes benzene-ethanol-water (I) and *n*-heptane-ethanol-water (II) in the range from 0 to 40 weight percents of (II).

In table II the densities and the refractive indices of the lower and of the upper phase are given.

TABLE II

Property	Lower phase	Upper phase
Density d_4^{20}	0·8772	0·8385
Refractive index n_D^{20}	1·3789	1·4640

At 20° C the volume of the lower phase constitutes 17·2 per cent of the total volume. This corresponds to 17·85 per cent when referring to the weight percentage.

References.

1) W. Świętosławski, »Ebulliometric Measurements«, pp. 18, 10, fig. 10. Reinhold Publ. Corp. New York, N. Y. (1945).
2) ibid p. 80, § 50.
3) ibid. p. 50, § 33.

Central Institute of Industrial Chemical Research. Warsaw, March, 1950.

Extrait du Bulletin de l'Académie Polonaise des Sciences et des Lettres
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O azeotropie czteroskładnikowym utworzonym z benzenu, etanolu, wody i izooktanu. — On the Quaternary Azeotrope Benzene-Ethanol-Water-Isooctane. II.

Note

de M. **W. ŚWIĘTOSŁAWSKI** et **K. ZIĘBORAK,**

présentée le 30 Mars 1950.

The general considerations given in the preceding paper (1) led us to the conclusion that isooctane should also form a quaternary azeotrope with benzene, ethanol and water. The structure of the 2,2,4-trimethylpentane would favor the formation of this azeotrope in spite of the fact that the boiling temperature 99·23 C (found for our sample) was slightly higher than that of normal heptane (98·60° C found in our case).

The experiments were to some extent facilitated because of the higher degree of purity of our sample. We found that the difference in the boiling and condensation temperatures determined by using the differential ebulliometer of standardized dimensions was 0·042°, so that the preparation belonged to the third degree of purity instead of being of the first degree as in the case of normal heptane. Knowing by analogy with the quaternary azeotrope described in the preceding paper the approximate composition of the quaternary azeotrope formed by isooctane, we prepared in advance a mixture of this composition and we submitted it to a careful fractional distillation using the ternary azeotrope benzene-ethanol-water as standard. The differential ebulliometer for purity test (2) was filled with this mixture and worked all the time while the fractional distillation was being carried out. The precision in condensation temperature measurements, after the corrections for the changes in barometric pressure had been introduced, did not exceed 0·004°. The azeotropic depression referred to the boiling temperature of the lower boiling ternary

azeotrope was found to be equal to 0·174°—0·178° C. This depression was greater by 0·10° C than that found in the case of the corresponding azeotrope formed by normal heptane with the same three components.

In table I numerical data are given showing the composition of the quaternary azeotrope as a whole (column I), of its lower phase (column II) and its upper phase (column III). In table II the densities and the refractive indices are listed.

TABLE I

Component	I Weight %	II Weight %	III Weight %
Benzene	61·5	11·5	72·2
Isooctane	14·1	1·2	17·0
Ethanol	17·7	54·6	9·9
Water	6·7	32·7	0·9
	100%	100%	100%

TABLE II

Property	Lower phase	Upper phase
Density d_4^{20}	0·8766	0·8293
Refractive index n_D^{20}	1·3782	1·4595

At 20° C the volume of the lower phase constitues 17·0 per cent of the total volume. This corresponds to 17·80 per cent when referring to the weight percentage

References

1) W. Świętosławski, K. Zięborak, Bull. Acad. Sci. Polonaise, 1950 A. 9.

2) W. Świętosławski, »Ebulliometric Measurements« p. 80 § 50, Reinhold Publ. Corp., New. York, N. Y. (1945).

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O azeotropie czteroskładnikowym benzen, etanol, woda i cykloheksan. — On the Quaternary Azeotrope Composed of Benzene, Ethanol, Water and Cyclohexane. III.

Note

de M. *K. ZIĘBORAK,*

présentée par M. W. Świętosławski le 30 Mars 1950.

In the preceding two papers (1, 2) the formation of the quaternary azeotropes have been described. Both these azeotropes are characterized by relatively small azeotropic depressions, when compared with the boiling temperatures of the lowest boiling ternary azeotropes. As is shown in the paper which follows (3), one could expect that cyclohexane would be able to form a quaternary azeotrope with benzene, ethanol and water and would be characterized by a greater difference between the boiling temperatures of the ternary azeotrope benzene-ethanol-water and the quaternary in which cyclohexane would enter as the fourth component. The same conclusion could be drawn from the fact that the boiling temperatures of two ternary azeotropes benzene-ethanol-water and cyclohexane-ethanol-water differ considerably less from each other than those which characterize the ternary azeotropes formed by ethanol and water with the two hydrocarbons mentioned: *n*-heptane and isooctane (2, 2, 4-trimethylpentane).

For carrying out the experiments relatively pure cyclohexane was submitted to seven fractional crystallizations. The boiling temperature of the purest fraction was found to be 80·60° C, compared with 80·119° C for benzene as standard. The ebulliometric purity test (0·049° for the difference between the boiling and condensation temperatures) showed that it was of the third degree of purity.

Two ternary azeotropes, benzene-ethanol-water and cyclohexane-ethanol-water were prepared by a careful fractional distillation and the main fractions were collected into two differential ebulliometers with standardized dimensions (4) the ebulliometric purity test of these azeotropes was examined (5) by measuring the differences between the boiling and the condensation temperatures of the two azeotropes. Values 0·005° and 0·130° were found. According to the ebulliometric scale of purity the ternary azeotrope containing benzene was of the fifth, the other containing cyclohexane of the first degree of purity. The assumption that the main contaminant in the azeotrope containing cyclohexane was benzene seemed to be very probable. If so, the benzene content could be determined when examining the increases in the difference between the boiling and condensation temperatures of the ternary azeotrope cyclohexane-ethanol-water produced by the increase in the amount of the ternary azeotrope in which cyclohexane was replaced by benzene. Into each of the two differential ebulliometers in which the main fractions of the two ternary azeotropes were brought to boiling, known amounts of another ternary azeotrope were successively added with the purpose of establishing the boiling and condensation temperatures of all the mixtures in which the amounts of both the ternary azeotropes changed from 0 to 100 percent. In Figure 1 the boiling and the condensation temperatures of all the mixtures are presented. The two starting points in the diagram, 64·86° and 62·73° C, correspond to the normal boiling and condensation temperatures of the two ternary azeotropes. As expected, the original difference $\Delta t = 0{\cdot}130°$ between the boiling and condensation temperature of the ternary azeotrope containing cyclohexane gradually decreases with the addition of the ternary azeotrope containing benzene. This was an indication that one of the impurities found in the cyclohexane sample was benzene.

The two curves shown in Figure 1 indicate distinctly that the quaternary azeotrope benzene-cyclohexane-ethanol-water was really found, and that the azeotropic depression referred to the boiling temperature of the lowest boiling azeotrope fluctuated within the limits from 0·52° to 0·53° C. The same depression calculated for the condensation temperature was 0·42°. It is difficult to conclude which value is closer to the real azeotropic depression.

It depends mostly upon the nature of the contaminations present in cyclohexane. If they form a quaternary azeotrope boiling lower than the quaternary azeotrope formed by cyclohexane, value 0·52°—0·53° C would be closer to the real azeotropic depression. On the contrary, if the contaminant is a higher boiling hydrocarbon, 0·42° C would be closer to that value.

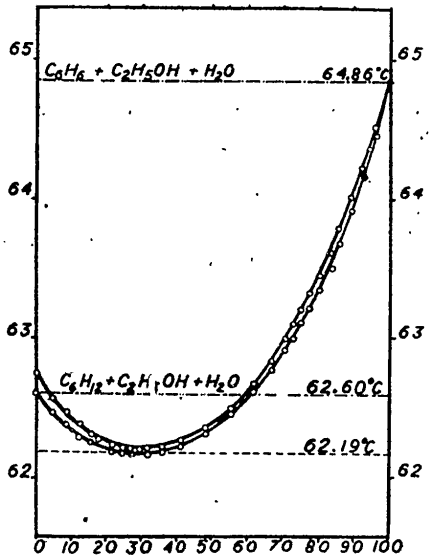

Fig. 1. Boiling and condensation temperatures of mixtures of azeotropes benzene-ethanol-water (I) and cyclohexane-ethanol-water (II) in the range from 0 to 100 weight percent of (II).

To prove which assumption is correct, the quaternary azeotrope under investigation was prepared by a careful fractional distillation by using as starting mixture that which had the compositon indicated by the point corresponding to the minimum on the curve. Values 0·41°C and 0·006° were found for the azeotropic depression and for ebulliometric purity test resulting from a direct comparison of the boiling and condensation tempe-

rature of the quaternary azeotrope. It was found that the sample was of the fifth degree of purity. Another experiment consisted in preparing by very careful fractional distillation a new sample of the ternary azeotrope cyclohexane-ethanol-water, which was found to be of the fifth degree of purity according to the ebulliometric test. When adding to that azeotrope the other one containing benzene, the minimum on the curve was found characterized by the azeotropic depression 0·41°C. Differences 0·006—0·012° between the boiling and condensation temperatures have characterized all the mixtures from the point representing the pure azeotrope cyclohexane-ethanol-water up to the other being right on the minimum.

The figures given below are:

1. Normal boiling temperature of the ternary azeotrope cyclohexane-ethanol-water 62·60° C.
2. Normal boiling temperature of the quaternary azeotrope cyclohexane-ethanol-water-benzene 62.19° C.
3. Composition of the quaternary azeotrope.

Component	Weight %
Cyclohexane	54·0
Benzene	21·5
Ethanol	17·4
Water	7·1

All the details of this investigation will be published in a paper dealing with the general problem of dehydration of ethanol by using mixtures of benzene and the so-called special narrow range gasoline fraction of Polish origin.

References.

1) See the preceding two papers.
2) See the preceding two papers.
3) See the two papers which follow.
4) W. Świętosławski, »Ebulliometric Measurements«, p. 18, fig. 10, Reinhold Publishing Corporation, New York (1945).
5) ibid, p. 80 § 49.

Central Institute of Industrial Chemical Research. Warsaw, March, 1950.

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1951

O zasięgach azeotropowych azeotropów dwu- i trójskładnikowych VI. — On the Azeotropic Ranges of two and three Component Azeotropes VI.

Note

de M. **W. ŚWIĘTOSŁAWSKI.**

présentée le 16 Mars 1951 par M. W. Świętosławski m. t.
et M. W. Kemula m. c.

Several months ago K. Zięborak and the author of this paper presented a series of papers (1), in which three quaternary azeotropes and the general conditions of the formation of ternary and quaternary azeotropes were described. The term azeotropic range of an agent with respect to a series $H_1, H_2 \ldots H_n$ of homologs, their isomers and compounds of very similar composition, was introduced. The usefulness of this term as well as of the expressions »tangent or almost tangent azeotropes and zeotropes« was proved.

Further investigations associated with the studies on ternary and quaternary azeotropes have stimulated us to extend the term azeotropic range to binary and ternary azeotropes. The following example may illustrate what should be kept in mind when examining the azeotropic range of an azeotrope.

Assume that agent A forms binary azeotropes with the series $H_1, H_2 \ldots H_n$, with the range $Z_A(H) = Z_g + Z_d$ where $Z_A(H)$ corresponds to the difference in boiling temperatures $t_{H_k} - t_{H_e}$ of two substances H_k and H_e characterized by tangent or almost tangent isobars when each separately mixed with agent A. Suppose that agents B and C form binary or ternary azeotropes with A: (A, B) and (A, B, C) on the one hand, and with the representatives of the series $H_1, H_2 \ldots H_n$ on the other. This means that the azeotropes (H_l, C) and (H_l, B, C) are formed, where H_l is one of the representatives of the series under consideration. In this case it may be expected that the azeotropes (A, B) (A, B, C)

under examination are also characterized by the azeotropic ranges $Z_{A,B}(H_l, B)$ and $Z_{A,B,C}(H_l, B, C)$ corresponding to the differences in boiling temperatures of two binary $t_{H_k,B} - t_{H_e,B} = Z_{A,B}(H_l, B)$ or two ternary azeotropes $t_{H_k,B,C} - t_{H_e,B,C} = Z_{A,B,C}(H_l, B, C)$ which form tangent or almost tangent isobars with the binary azeotrope (A, B) or with the ternary (A, B, C).

In fig. 1 the simple scheme of the formation of the binary azeotropes A, H_l is shown. It is clear from the graph that the

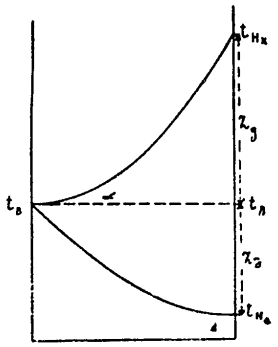

Fig. 1.

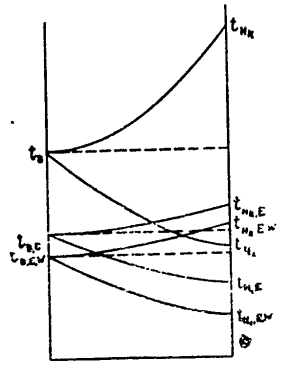

Fig. 2.

azeotropic range $Z_A(H)$ is composed of two sections, $Z_A(H) = Z_d + Z_g$, where Z_g is the lower and Z_g the upper part of the range. Fig. 2 corresponds to the scheme in which the general case of the formation of three series of azeotropes (A, H_l), (A, B, H_l) and (A, B, C, H_l) is graphically represented. For simplicity it is assumed that the azeotropes of all the types, (A, H_l), (A, B, H_l) and (A, B, C, H_l), form tangent or almost tangent isobars having the same components H_k and H_e (see fig. 2). In fact it was mentioned in one of the previous papers (2), that relatively small shifting might occur. In principle, however, the whole scheme (with some insignificant changes) may be accepted as representing the real relations between the binary, ternary and quaternary azeotropes formed by agents A, B and C with the series $H_1\ H_2 \ldots H_h$ of homologs, their isomers and other closely related compounds.

Main and secondary azeotropic agents

Suppose that we examine the concentrations of each of the substances forming binary, (A, H_i), ternary (A, B, H) and quaternary (A, B, C, H) azeotropes with the series $H_1, H_2 \ldots H_n$, in which H is one of the representatives of this series. The azeotropic agent A characterized by the lowest azeotropic range $Z_A(H)$:

$$Z_A(H) < Z_B(H) < Z_C(H)$$

will be called below the main azeotropic agent and the other two agents B and C, the secondary azeotropic agents. This classification is essential for the proper understanding of the role played by these agents and the relations which exist in the concentration changes of each of the components in the series of ternary and quaternary azeotropes examined.

In fact, it can be seen from the graph, that the concentration of component A changes from its highest concentrations at points $t_A, t_{A,B}, t_{A,B,C}$ in which tangent isobars are formed with H_k, (H_k, B) and (H_k, B, C), respectively, and it reaches its zero values in points t_{H_e}, $t_{H_e,B}$ and $t_{H_e,B,C}$ at which substance A or its corresponding azeotropic mixtures with B or with B and C form tangent isobars at these points.

The highest concentration of A at t_A is 100 per cent, at $t_{A,B}$ it corresponds to the concentration of A in the binary azeotrope (A, B), and at $t_{A,B,C}$ to that in the ternary azeotrope (A, B, C).

The same concerns the concentrations of component H_i, which represents each time one of the substances of the series from H_e to H_k. As for the highest boiling representative H_k, its concentration is equal to zero per cent at points t_A, $t_{A,B}$ and $t_{A,B,C}$ (fig. 2), and the concentration of the lowest boiling substance H_e is equal to hundred per cent at t_{H_e} and to the concentrations found in the binary azeotrope (H_e, B) at point $t_{H_e,C}$ and in the ternary azeotrope (H_e, B, C) at point $t_{H_e,B,C}$. The concentrations of other compounds lying in the series between H_k and H_e increase gradually within the limits given above.

Quite different is the role of the two secondary azeotropic agent B and C. They may be considered as agents accompany-

ing the main components, which are the main agent A and the substances of the series $H_1, H_2 \ldots H_n$. Agent B is present as the third component in all the ternary azeotropes of the type (A, B, H_l) and its concentration undergoes relatively small changes, depending to a large extent upon the boiling temperature of the azeotrope. The replacement of H_l in the series by another, say H_h, exerts an insignificant effect on the change in concentration of component B. The same may be noticed concerning the fourth component C in quaternary azeotropes of the type (A, B, C, H_l) The changes in concentration of both the secondary azeotropic agents depend mostly upon the boiling temperature but not upon the nature of the component H_l or upon the concentrations of A and H_l in the series embracing the whole azeotropic range $Z_{A,B,C}(ABH) = t_{A,B,C,H_h} - t_{A,B,C,H_l}$.

The usefulness of the new terms introduced and the proof of the scheme shown in fig. 2 may be seen when examining the case of three quaternary azeotropes composed of benzene, ethanol and water as three common constituents of three quaternary azeotropes (B, E, W, H_l) in which B stands for benzene, E — for ethanol, W — for water, and H_l is one of the three hydrocarbons: normal heptane, isooctane (2,2,4-trimethylpentane) or cyclohexane. In Zięborak's paper, which follows, the scheme shown in fig. 2 is replaced by another in which the six substances mentioned above play their role in forming three quaternary azeotropes.

From the considerations given above it may be concluded that empirical equations may be found for establishing the concentrations of A and H_l and the boiling temperatures of the ternary (A, B, H_l) and quaternary (A, B, C, H_l) azeotropes in a similar way as has been done for binary azeotropes composed of agent A and series of homologs $H_1, H_2 \ldots H_n$. As for the changes in concentration of the secondary azeotropic agents B and C, the establishment of empirical equations seems to be a simpler problem. The number of ternary and quaternary azeotropes of the type considered in this paper is too small for the undertaking of such a calculation. More facts should be established and further series of homologs should be examined in order to prove definitely that we are following the right way.

Summary

1. The term azeotropic range has been extended to include binary and ternary azeotropes formed by an agent A and a series of homologs, their isomers and closely related substances.

2. The term main azeotropic agent is used for the substance characterized by the lowest value of the azeotropic range.

3. The term secondary agents is suggested for those components B and C which form ternary and quaternary azeotropes of the type $(A, B. H_l)$ and (A, B, C, H_l) where H_l is one of the substances of the series $H_1, H_2 \ldots H_n$.

4. It is shown that A and H_l replace each other wholly or in part in the series of ternary and quaternary azeotropes. Component B is always present in all azeotropes of the type (A, B, H_l) or C and B in quaternary azeotropes (A, B, C, H_l). Their concentrations depend mostly upon the boiling temperature of the azeotrope and to a smaller extent upon the nature of A and H_l.

5. A scheme is presented which illustrates in a clear manner the conditions under which binary, ternary and quaternary azeotropes of the types (A, B, H_l) and (A, B, C, H_l) may be formed.

Central Institute of Industrial Research, Physico-chemical Laboratory, University of Warsaw.

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1951

O azeotropach czteroskładnikowych utworzonych przez węglowodory parafinowe i naftenowe z benzenem, etanolem i wodą. VII. — On the Quaternary Azeotropes Formed by Paraffinic and Naphthenic Hydrocarbons with Benzene, Ethanol and Water. VII.

Note

de M. **K. ZIĘBORAK,**

présentée le 16 Mars 1951 par M. W. Świętosławski m. t.
et W. Kemula m. c.

In a series of papers on ternary and quaternary azeotropes (1), three articles have dealt with quaternary azeotropes obtained by a careful rectification of mixtures of benzene, ethanol, and water with *n*-heptane, 2, 2, 4-trimethylpentane (isooctane) or cyclohexane respectively. These investigations have been initiated after a series of fractional distillations of a mixture of gasoline, containing hydrocarbons boiling in the range from 93° to 109°C (according to Engler 96° to 103°C), with benzene (*B*), ethanol (*E*), and water (*W*), have indicated that a series of quaternary azeotropes of the type (*B*, *E*, *W*, H_l) has been formed in the column and collected in the receiver. The purpose of this paper is to present on one diagram the data obtained and to submit a discussion on the phenomena observed.

The experiments consisted in adding to the ternary azeotrope (*B*, *E*, *W*) successively known amounts of another ternary azeotrope (H_l, *E*, *W*), where H_l stands for *n*-heptane, isooctane or cyclohexane respectively. In some particular cases, e.g. when cyclohexane was used as the fourth component, known amounts of the azeotrope (*B*, *E*, *W*) have been added to the azeotrope cyclohexane-ethanol-water. In figure 1 the corresponding diagram is shown. Details of the performance of the experiments and all numerical data will be published elsewhere (3). The analysis of the graph shows that the quaternary azeotrope benzene-ethanol-water-*n*-heptane may be considered as almost tangent. In fact

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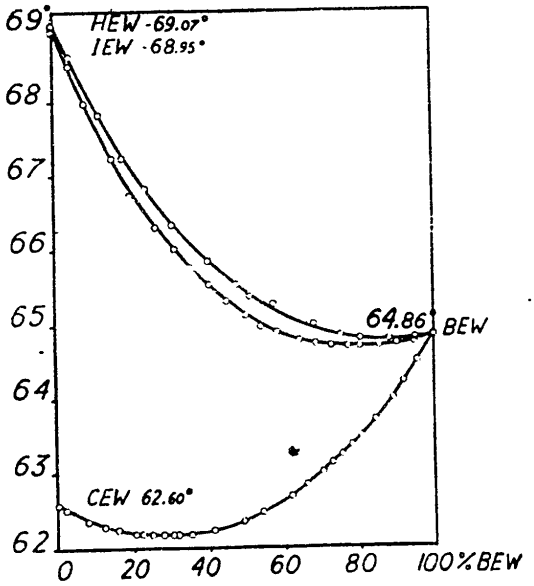

Fig. 1.

derably higher boiling temperatures than *n*-heptane, it should be concluded that the quaternary azeotrope under consideration is the last in the upper part of the diagram. The quaternary azeotrope 2, 2, 4 trimethylpentane-benzene-ethanol-water is characterized by a somewhat higher value of the azeotropic depression: $\Delta t = t_{B,E,W} - t_{B,E,W,H} = 0{\cdot}170°C$.

The third quaternary azeotrope with cyclohexane as the fourth component is characterized by a considerably lower normal boiling

temperature. If we call azeotropic depression the difference between the lower boiling ternary azeotrope and the quaternary one, then we find that the azeotrope benzene-ethanol-water-cyclohexane boils at a temperature 0·41°C lower than the ternary one composed of cyclohexane- ethanol- water. It is evident from the graph that the fourth component H_x of the azeotrope $(B, E. W, H_x)$, which will be characterized by a tangent or almost tangent isobar, should boil in the range from 68° to 72°C.

If we assume that the boiling temperature of hydrocarbon H_x is equal to 68°C, it would practically coincide with the tangent binary azeotrope (B, H) formed by benzene and H_x.

The scheme shown in fig. 1 demonstrates the usefulness of using the term azeotropic range not only for the individual chemical compounds $t_A(H)$ with respect to a series of homologs and their isomers $H_1, H_2 \ldots H_n$, but also for binary and even ternary azeotropes, In this way the azeotrope (A, B) may be characterized by a range $Z_{A,B}(H, B)$ with respect to a series of binary azeotropes (H_1, B), $(H_2, B) \ldots (H_n, B)$ etc. In the preceding paper (2) this idea has been discussed in general terms. From the considerations given in this paper it follows that the concentrations of benzene and the hydrocarbons playing the role of the fourth component replace one another in the series of quaternary azeotropes. For this reason Świętosławski suggested that benzene should be called the main azeotropic agent (2). The concentrations of ethanol and water undergo changes within very restricted limits. In some cases the precision of the analysis does not permit the establishment of any regularity, which might be expected on the basis of the theoretical considerations.

Below a table is given in which the azeotropic concentrations of benzene, ethanol, water and the fourth component are listed.

Concentrations of components in quaternary azeotropes.

Component	% Cyclohexane	% 2 2, 4 Trimethyl-pentane	% *n*-heptane
Benzene	21·5	61 5	62·4
Ethanol	17·4	17·7	18·7
Water	7·1	6·7	6·8
Fourth component	54·0	14 1	12·0

The columns containing numerical data are headed by the name of the fourth component.

From the table given above the following conclusions may be made:

1. The concentration of benzene increases with the increase in boiling temperature of the quaternary azeotrope.

2. The concentration of the fourth component decreases with the increase in boiling temperature of the quaternary azeotrope.

3. The concentration of ethanol undergoes a slight increase when passing from cyclohexane through 2, 2, 4 trimethylpentane to normal heptane.

4. No regularities can be found for the change in concentration of water. The latter may be explained by difficulties encountered in carrying out the analysis. The concentration of water is found from the difference $100 - \Sigma c_i$, where c_i represents the concentrations of all the remaining three components.

It is very probable that the concentrations of water should exhibit a slight increase in the same way as the concentrations of ethanol, because the contents of these agents, called by Świętosławski »secondary« or »accompanying« agents, depend primarily upon the boiling temperature of the azeotropes.

Central Institute of Industrial Research and Physico-chemical Laboratory, University of Warsaw

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Classe des Sciences Mathématiques et Naturelles — Série A: Sciences Mathématiques
— 1951 —

On the Method of Azeotropic Range Determination. VIII.

by

W Świętosławski and A. Orszagh

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Classe des Sciences Mathématiques et Naturelles — Série A: Sciences Mathématiques
1951

O metodzie oznaczania zasięgów azeotropowych. VIII. On the Method of Azeotropic Range Determination. VIII.

Note

de MM. **W. ŚWIĘTOSŁAWSKI** and **A. ORSZAGH**,

présentée le 16 Mars 1951 par W. Świętosławski m t
et M. W. Kemula m. c.

1. Azeotropic ranges and their significance

In one of the previous papers on azeotropy (1) the usefulness of the term azeotropic range of agents with respect to a series H_1, $H_2 \ldots H_n$ of homologs, their isomers and other chemically related and similar compounds has been shown. For convenience in fig. 1 the general scheme is presented, in which not only the azeotropic range $Z_A(H)$ of agent A with respect to the series of substances (H) but also the azeotropic ranges $Z_{A,B}(H,B)$ and $Z_{A,B,C}(\mathrm{H,B,C})$ of the binary and ternary azeotropes (A,B) and (A,B,C) with respect to the series of binary $(H_i B)$ and ternary (H_i, B, C) azeotropes are shown. In the last two cases, the ranges $Z_{A,B}(H,B)$ and $Z_{A,B,C}(H,B,C)$ correspond to the differences:

$$Z_{A,B}(H,B) = t_{H_k,B} - t_{H_e,B}$$

$$Z_{A,B}(H,B,C) = t_{H_k,B,C} - t_{H_e,B,C}$$

provided that in all cases we have the same representatives H_k and H_e which either alone or accompanied by B or by B and C form tangent or almost tangent isobars with A and with the azeotropes (A,B) and (A,B,C): respectively. Let us remember that agent A, characterized by the lowest value of the azeotropic range $Z_A(H)$, as compared with the ranges $Z_A(H)$ and $Z_C(H)$ may be called the **main** azeotropic agent (1). The two other substances, B and C, are called »secondary azeotropic agents«. They accompany all the ternary and quaternary azeotropes formed by the

binary ones (A, B) and (H_l, B) on the one hand and (A, B, C) and (H_l, B, A) on the other. The reason why such a definition seems to be convenient is given in paper VI of the same series of communications on azeotropy.

It is easy to understand that difficulties would be encountered if it were intended to determine the azeotropic ranges of some substances with respect to the series (H). In fact one would be forced to use a relatively large number of pure representatives of the series (H) in order to measure the azeotropic depressions and concentrations for those azeotropes. Taking this experimentally collected material as a basis it would be possible to extrapolate the boiling temperature of the two representatives H_k and H_e which form tangent or almost tangent isobars with A. The problem becomes even more complicated if it is desired to find the azeotropic ranges of the binary or even ternary azeotropes $Z_{A,B}(\mathrm{H, B})$ and $Z_{A,B,C}(\mathrm{H, B, C})$. For this reason, for some time we have been using another method which is characterized by simplicity in operation and by usefulness in its practical application.

2. Determination of the azeotropic ranges of agents forming azeotropes with hydrocarbons

The azeotropes formed by paraffinic, naphthenic and aromatic hydrocarbons are the most important on account of their numerous practical applications. This is why we have paid much attention to different fractions of gasoline and petroleum fractions constituting a natural source of the series $H_1, H_2 \ldots H_n$ of homologs, their isomers and chemically similar compounds. We now very often use these mixtures for determining the two boiling temperatures, the first at which the azeotropes with agent A start to be formed and the second at which no more azeotropes (A, H_l) can be found in the distillate. In doing so we can follow two different ways: first by the chromatographic method we can remove from the gasoline all the aromatic hydrocarbons present in it, secondly, we can neglect the influence of small percentages of aromatic hydrocarbons and we can apply either gasoline mixtures or of those containing higher boiling hydrocarbons without purification. Experiments proved that different petroleum fractions, including petroleum ether and gasoline, could be directly

used. The differences in the azeotropic concentrations and boiling temperature depressions of naphthenes when compared with those observed in the series of paraffins are in the case of the ternary (A, B, H_l) and quaternary (A, B, C, H_l) azeotropes so small that they do not change in any appreciable manner the values found

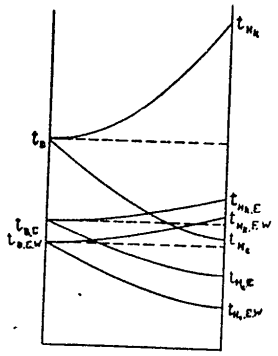

Fig. 1. Scheme showing the formation of binary, ternary and quaternary azeotropes by agents A, B, and C with a series of homologs and their isomers. $Z_A(H)$, $Z_{A,B}(H, B)$ and $Z_{A,B,C}(A, B, C)$ are the azeotropic ranges of the substances A and of two azeotropes (A, B) and (A, B, C).

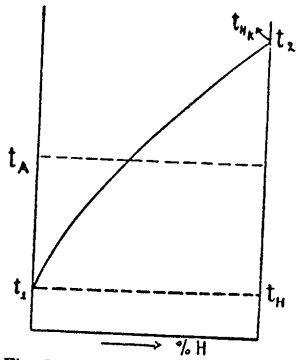

Fig 2. Distilling curve $(\%\ H, t)$ of a mixture of homologs and their isomers and chemically related substances.; t_A represents the boiling point of the azeotropic agent; t_1 and t_2 the temperatures at the start and at the end of the distillation.

or extrapolated for those mixtures which are classified as tangent or almost tangent azeotropes. These remarks were necessary before the description of the method used could be given.

Let us assume that the shape of the distilling curve of gasoline has been established by plotting the condensation temperatures of the distillate against the volume or weight percentage of the fractions (fig. 2). Suppose that the column is characterized by a reasonably high number of theoretical plates and that the reflux ration 10 1 was kept constant. Suppose that the distillation started at t_1°C and was completed at t_2°C, and that the density as well as the refractive index graphs of the frac-

tion collected were drawn on the same diagram. Now we use the same quantity of gasoline and we add to it a known amount of the agent *A*, the azeotropic range of which we intend to measure. Then we carry out the distillation in the same device establishing as before the same reflux ratio.

Depending upon the upper t_{H_k} and the lower t_{H_e} temperature of the azeotropic range $Z_A(H)$ of agent *A*:

$$Z_A(H) = t_{H_k} - Z_{H_e}$$

we may observe three characteristic cases. All of them are represented in figs. 3, 4 and 5.

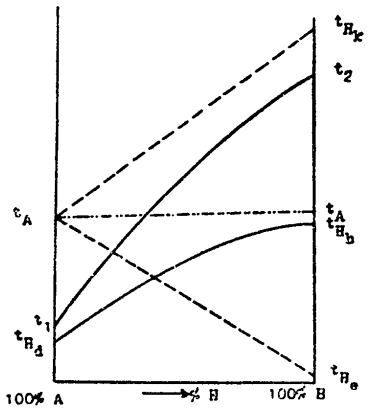

Fig. 3. Distilling curve (t_{H_d}, t_{H_k}) showing the change in condensation temperatures of a mixture of binary azeotropes (A, H_I) plotted against the percentage of mixture (%, *H*) collected in the receiver. Agent *A* is characterized by a very large azeotropic range $Z_A(H)$.

For direct comparison the distilling curve of the mixture of gasoline with agent *A* is drawn in an unusual manner, i. e. we plot the condensation temperature against the amount of gasoline and not of the gasoline and agent *A* found in each of the fractions collected. For this reason each time we should determine the composition of the fraction in order to substract the amount of *A* in that fraction. In doing so we are able to compare direc-

tly the two distilling curves under examination. In this way the same points on the abscissa axis correspond to the amounts of hydrocarbons collected, in spite of the fact that in the course of the second distillation different and often relatively large amounts of agent *A* are present in the distillate.

Let us consider three typical cases encountered very often. In case I the azeotropic range $Z_A(H)$ is so large that all of the

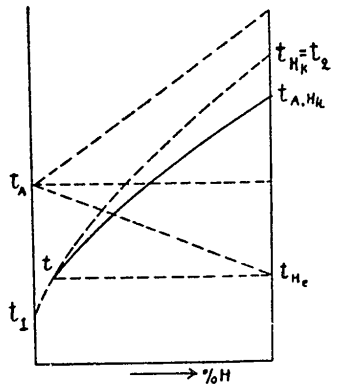

Fig. 4. Diagram similar to that shown in fig. 3, with the difference that the lower branch of the azeotropic range starts at point t_{H_e}, lying somewhat higher than t_1. The upper end of the curve lies below t_{H_A}, indicating that the upper end of the range $Z_A(H)$ lies somewhat higher than t_2.

hydrocarbons found in the gasoline used form binary azeotropes with agent *A*. It is easy to predict that the distilling curve of the mixture of gasoline with *A* will lie below the distillation curve of the gasoline itself. This case is schematically represented in fig. 3.

For this reason, for determining the azeotropic range $Z_A(H)$ a mixture containing hydrocarbons with considerably lower and higher boiling temperatures should be used. It may happen that instead of the curves shown in fig. 3 another, represented in fig. 4, will be obtained. In this case the lower point of the azeotropic

range t_{H_e} may be found. The gasoline examined contains in addition some hydrocarbons boiling too low to form azeotropes.

The third case corresponds to the conditions under which the azeotropic range $Z_A(H)$ may really be found (fig. 5).

Curve $t_{H_e}O, B$ should be considered as typical. In fact, when starting the distillation of a mixture of A with a petroleum or gasoline fraction, a certain decrease in the condensation temperature of the distillate may be observed.

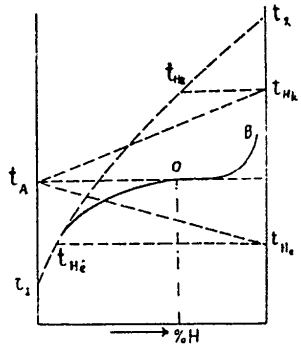

Fig. 5. Diagram similar to the two preceding, with the difference that point O is a transition one showing that the tangent azeotrope $t_{A,Hk}$ has been formed. From point O to the right side of the curve almost tangent zeotropes of A with the series of representatives boiling above t_{H_k} have been distilled off.

At a given point the curve shown in fig. 5 becomes tangent to the horizontal line drawn through the point representing the boiling temperature of agent A; afterwards it should cross this line and show a steady increase in the condensation temperature. In most typical cases, however, it is not so. Before large temperature increases are noted, section OB of the curve is observed which corresponds to the formation of almost »tangent zeotropes« This phenomenon has been described in one of the previous papers of this series. (V).

When continuing the distillation small gradual increases in condensation temperatures will be noticed. The distillate will contain large amounts of A and relatively small but steadily increasing quantities of higher boiling hydrocarbons. This takes place until the components characterized by large deviations of their mixtures with A from Raoult's law are exhausted. After reaching this point, considerable temperature increases will be observed, as shown in the last part of curve $t_{H_e}OB$ represented in fig. 5. This should be considered as a proof that points lying far from the tangency to the horizontal line drawn through t_A have been reached.

It is probable that in other systems the shape of curve $t_{H_e}OB$ will differ from what we have noticed up to date. The number of systems examined is too small for any generalization.

3. Determination of azeotropic ranges characterizing binary and ternary azeotropes

In one of our previous papers (VI) on azeotropy the suggestion was made that the term azeotropic range of binary and ternary azeotropes should be used. This is based on the fact that the concentrations of secondary azeotropic agents undergo small changes in the whole series of ternary and quaternary azeotropes (A, B, H_l) and $(A, B, C\ H_l)$, respectively, formed by the binary (A, B) and ternary (A, B, C), azeotropes with (H_l, B) and (H_l, B, C). As in the previous considerations H_l designates one of the substances of the series $H_1, H_2 \ldots H_n$. For the corresponding ranges the following symbols are suggested: $Z_{A,B}(H_l, B)$ and $Z_{A,B,C}(H_l, B, C)$ for the azeotropes mentioned above.

They show that the binary azeotrope (A, B) may form, in some limits of boiling temperatures of the binary azeotrope (H_l, B), ternary azeotropes (A, B, H_l) and that the ternary azeotrope (A, B, C) may form, with the same limitation, quaternary (A, B, C, H_l) ones.

A method quite similar to that described in the preceding paragraph may also be used.

A system examined in detail is described below. Let us suppose that we want to determine the azeotropic range of a ternary azeotrope composed of benzene (B), ethanol (E) and water (W) with respect to the ternary azeotropes formed by representatives of the series $H_1, H_2 \ldots H_n$ found in the appropriately chosen fraction of gasoline with ethanol and water.

First, the distillation of a mixture of gasoline with an excess of ethanol (E) and water (W) should be carried out to establish the shape of the distilling curve of the ternary azeotropes (H_l, E, W). Suppose that curve I corresponds to the distillation of that mixture (fig. 6). The distillation started at $t_{H,E,W}$ and was completed at the temperature $t_{H_n,E,W}$. Afterwards we carry out another distillation after adding an excess of benzene to the same mixture of gasoline, ethanol and water. Suppose that curve II represents graphically this distillation. After the lower limit of the

azeotropic range has been reached, the upper portion of the distilling curve starting at point D (fig. 6) transforms itself into one similar to the curve AOB shown in fig. 5. In fact, it is tangent

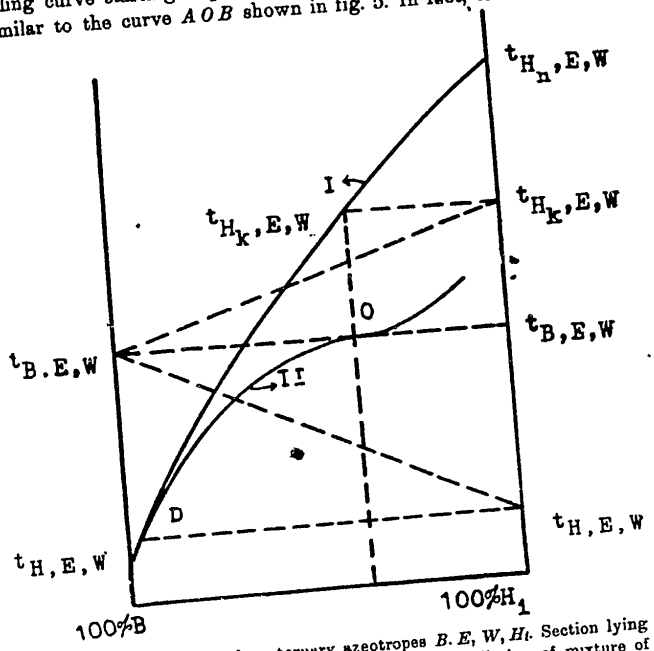

Fig 6. Distilling curve of quaternary azeotropes $B.E, W, H_l$. Section lying to the right of point O represents the zeotropic distillation of mixture of ternary azeotrope B, E, W with ternary azeotropes H_l, E, W.

to the horizontal line drawe through the point representing the boiling point of the ternary azeotrope $t_{B,E,W}$ composed of benzene, ethanol and water (64·86°C). This point corresponds to the upper limit of the azeotropic range of this ternary azeotrope with respect to the series $H_1, H_2 \ldots H_n$ of homologs and their isomers, forming the ternary azeotropes $(H_l EW)$. In previous papers of this series of articles 2, 2, 4 trimethylpentane and n-heptane represented two paraffinic hydrocarbons which formed with ethanol

and water two ternary azeotropes characterized by almost tangent isobars with ternary azeotropes composed of benzene-ethanol- and water. On the other hand, benzene forms a almost tangent isobar in mixtures with *n*-heptane or 2, 2, 4 trimethylpentane. Large deviations from Raoult's law are found along all the concentrations of these binary mixtures. Taking these facts as a basis, we may conclude that the range of the azeotrope (B, E, W) is limited by the ternary azeotropes (H, E, W) and (H_1, E, W) in which H and H_1 are the same hydrocarbons or at least are close neighbours of those which form tangent or almost tangent isobars with benzene. We do not think that such a case is typical. The existence of other mixtures differing from those mentioned above may be found.

It must be emphasized that the experimental technique in studying mixtures of binary, ternary and sometimes quaternary azeotropes should be based on that described in the book »Ebulliometric Measurement«. The principle of comparative measurements should be respected and standard substances or azeotropes for the direct comparison of boiling and condensation temperatures should be used. For this reason the ebulliometers containing standard liquids should be located side by side with the head of the distilling column. Very often the main fraction consisting of a pure binary or ternary azeotrope should be directly collected into the differential ebulliometer for purity test determination or for using as a standard for direct comparison with another liquid. Two electric resistance thermometers or two mercury thermometers of the Beckmann or Roberteau type should be used and transferred from time to time from one thermometer well into another so as to measure the differences in boiling or condensation temperatures with an accuracy not less than $\pm 0{\cdot}003 \pm 0{\cdot}006$°C.

It may be assumed that the upper limit of the azeotropic range O (fig. 5) is reached, if the condensation temperature measured in the thermometer well placed in the head of the distilling column is equal to that determined for the pure azeotropic agent. The lower limit of the azeotropic range may be determined on the basis ex. e. $B, (B, E)$, (B, E, W), respectively of the composition of the fractions collected in the course of the distillation. The appearance of the main azeotropic agent in any measurable

quantities in the fraction collected should be considered as evidence that the lower limit of the azeotropic range has been reached. In the case considered above, point D is reached when the quaternary azeotrope (B, H, E, W) is found in the receiver This takes place when the fraction collected contains small, but measurable quantities of benzene. To get a definite proof that quaternary azeotropes have been really formed, direct experiments should be carried out with pure compenents boiling at the corresponding temperatures. In the case of benzene, ethanol and water the lower boiling hydrocarbon should boil at $68-72°C$. As to the upper one, n-heptane should be considered as the last component forming quaternary azeotropes of the type (B, E, W, H_l).

4. Influence of the presence of naphthenic hydrocarbons

All specimens of gasoline which were used in our investigations contained some amounts of naphthenic hydrocarbons; cyclohexane and isomeric methylpentanes especially were always present. It could be suspected that they might have exerted an unfavorable influence on the results obtained. We have noticed, however, that their influence was insignificant. In order to control the measurements it was necessary to determine as often as possible the refractive indices and the densities of the fractions collected. The known fact that the naphthenes are characterized by higher values of refractive indices and of densities has helped us to find out whether in critical points near D and O (fig. 6) unusually high refraction and density of the fractions collected were observed. In our experiments we did not notice those phenomena. If more accurate determinations of azeotropic ranges are carried out, the naphthenic hydrocarbons should be removed, e. g. by the selective adsorption chromatographic method (2). On the contrary it is not easy to remove isomeric paraffins or to operate exclusively with the normal ones.

5. General remarks

More systematic investigations have to be carried out in order to prove the applicability of the method for determining the azeotropic ranges of quite different systems. It is, however, very convenient for the determination in certain mixtures of homologs

and their isomers (H) not only of the azeotropic range $Z_A(H)$ characterizing the agent A, but also of the ranges $Z_{A,B}(H,B)$ and $Z_{A,B,C}(H,B,C)$ containing the secondary azeotropic agents B and C. The method of successive comparative measurements becomes a very useful means of carrying out experiments following each other under identical conditons. In this way it is possible to get direct answers to all the questions associated with problems dealing with systems composed of a number of binary, ternary and quaternary azeotropes.

Summary

1. A method for approximate determination of the azeotropic range $Z_A(H)$ of an agent A with respect to the series $H_1, H_2 \ldots H_n$ of homologs, their isomers and other chemically relative substances is described.

2. It has been proved that this method may also be applied for the determination of the azeotropic range $Z_{A,B}(H,B)$ of the binary azeotrope (A,B) with respect to the series of binary azeotropes (H_1,B), $(H_2,B)\ldots(H_n,B)$ composed by a secondary azeotropic agent B with the series $H_1, H_2 \ldots H_n$, mentioned in point 1.

3. If quaternary azeotropes of the type (A,B,C,H_l) exist, the method may be used for determining the azeotropic range $Z_{A,B,C}(H,B,C)$ of the ternary azeotrope (A,B,C) with respect to the series of ternary azeotropes of the type (B,C,H_l), in which H_l is one of the representatives of the series found between H and H_n.

4. Details are given on how to carry out the experiments according to the method described. Three different cases are examined. In the first, the azeotropic range Z_A(H) is so large that binary azeotropes (A,H_l) are formed by the agent with all the substances present in the mixture $H, H_2 \ldots H_n$. In the second case, some lower boiling substanees do not form binary azeotropes with A. The third case is characterized by a low value of the azeotrope range so that some lower and higher boiling representatives of the series do not form azeotropes with A. The same phenomena may be noticed in the case of binary and ternary azeotropes of agent A and of other representatives of the series $H_1, H_2 \ldots H_n$ with secondary agents B and C.

5. An example is given of the formation of a series of quaternary azeotropes composed of benzene, ethanol, water and hydrocarbons contained in fraction 68—99°C of gasoline.

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Janvier Décembre 1950

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CL. III - Vol. I, Nos 1—2, 1953

CHEMISTRY

Classification of Negative Azeotropes XIV

by

W. ŚWIĘTOSŁAWSKI

Communicated at the meeting of September 22, 1952

1. Negative Azeotropes. We call negative binary azeotrope a mixture of two liquids which form an isotherm with a minimum vapour pressure. The number of known negative azeotropes is not as large as that of positive ones. In spite of this they play an important role in the understanding of the phenomena which take place when different kinds of liquid mixtures are submitted to a fractional distillation. Their significance increases with the discovery of a large number of ternary positive-negative azeotropes which constitute the subject of the next paper in this series. In order to give an adequate explanation of the phenomena which take place when a negative binary azeotrope forms with a third component a ternary positive-negative one, the classification of binary negative azeotropes seems to be of considerable importance.

2. Three Groups of Negative Azeotropes. It is generally accepted that a minimum vapour pressure appears if the attractive forces a_{11} and a_{22} acting between molecules of each of the component 1 and 2 are weaker than those a_{12} acting between two different molecules:

$$a_{11} < a_{12} > a_{22}.$$

In spite of this, a relatively large number of negative azeotropes are known in which, besides van der Waals' forces, chemical or electrochemical ones are responsible for the formation of minimum vapour pressures and maximum boiling points. Taking this into consideration the following classification of binary negative azeotropes composed of components other than water may be accepted. According to this classification the negative azeotropes should be divided into three groups: to the first group belong binary negative azeotropes in which the inequality between van der Waals' forces:

$$a_{11} < a_{12} > a_{22}$$

is responsible for the appearance of a minimum vapour pressure. A relatively large number of negative azeotropes of this group is known, e. g. chloroform and acetone, pyridine and some of the alcohols, etc.

To the second group belong all dehydrated mixtures composed of a weak acid and a weak base.

As yet, only a relatively small number of these mixtures has been carefully examined. Among them, azeotropes formed by acetic acid or phenol and different aromatic bases, especially pyridine and its homologues, are listed in two Horsley's, and in Lecat's, tables.

The third group comprises mixtures of a weak base with a strong acid or a weak acid with a strong base.

Up to now, the properties of several mixtures belonging to the third group have been examined but not as azeotropes. They have been treated rather as salts. For instance pyridine and its homologues, as well as some aromatic amines, form volatile hydrochlorides which may be submitted to fractional distillation. In solutions and in the solid phase they behave as salts formed by equivalent amounts of the two components. For this reason they have not been listed in the tables as negative azeotropes. The phenomena are quite different if the hydrochlorides mentioned above are submitted to fractional distillation. Under constant pressure they boil and distill at constant temperatures but, in spite of this, their distillation products do not correspond to the composition of salts. They contain more hydrogen chloride than salts do. That is why they should be treated rather as binary negative azeotropes. Because of the chemical forces involved, the increases in the boiling points of the corresponding negative azeotropes are very high compared with the increases in the boiling points of two other groups of these azeotropes. Usually their boiling points are more than one hundred degrees higher than the corresponding bases. For this reason they must be considered as interesting subjects for examination as azeotropic agents.

We hope soon to be able to present the results of some experiments with these azeotropic agents.

In the note which follows, representatives of all three groups of binary negative azeotropes are examined with respect to the formation of so-called saddle or ternary positive-negative azeotropes.

SUMMARY

Negative binary azeotropes composed of components other than water have been divided into three groups. This classification is based on different types of intermolecular forces responsible for the appearence of the minimum vapour pressures and the maximum boiling temperatures. To the first group belong azeotropes in which the molecules of the two components attract each other with larger van der Waals' forces than those with which the molecules of one component are attracted. To the second group belong dehydrated mixtures of weak bases and weak acids. The third group is composed of dehydrated mixtures of weak bases and strong acids and vice versa.

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CHEMISTRY

Binary Eutectics Formed by One Component with a Series of Homologues

by
T. PENKALA

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of January 12, 1953

Several years ago W. Świętosławski [1] published a paper in which a series of binary eutectics, formed by a certain compound with a series of chemically quite different substances, were presented in one diagram. It was found that the eutectic points lay practically on a monotonic, continuous curve. Basing himself on this observation, Świętosławski came to the conclusions that if eutectics formed by component A with a series (B) of

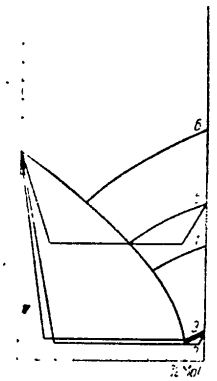

Fig. 1

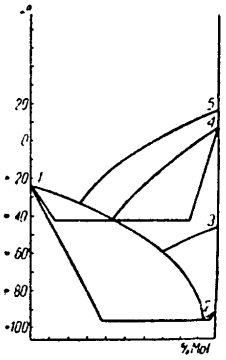

Fig. 2

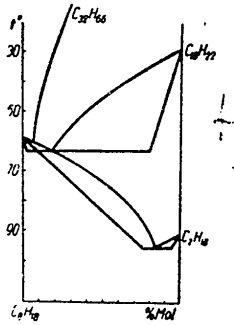

Fig. 3

Fig. 1. Eutectics formed by benzene (1) with toluene (2), ethyltoluene (3), metaxylene (4), orthoxylene (5) and paraxylene (6), according to Kravchenko's observations

Fig. 2. Eutectics formed by orthoxylene (1) with toluene (2), metaxylene (3), benzene (4) and paraxylene (5)

Fig. 3. Eutectics formed by paraxylene (1) with toluene (2), ethylbenzene (3), metaxylene (4), orthoxylene (5) and benzene (6)

homologues were examined, the curve on which the eutectic points would lie, would form a common curve corresponding to the well known freezing curve.

This note gives a series of examples which not only confirm Świętosławski's suggestion, but also lead to its further extension to those systems in which the eutectics are formed by two solid solutions, and not by two pure components, coexisting with the liquid phase in ideal eutectic systems.

In Figs. 1, 2 and 3 illustrations are given proving the correctness of Świętosławski's statements and of their further extension.

The examples given above refer to systems formed exclusively by different combinations of homologues of benzene and by benzene itself. A number of other examples have been found and will be described in a paper to be published in "Roczniki Chemii".

In the case of systems formed by paraffinic hydrocarbons: (C_6H_{14}, C_7H_{16}), (C_8H_{18}, $C_{10}H_{22}$), ($C_{10}H_{22}$, C_8H_{18}), ($C_{10}H_{22}$, C_7H_{16}) the eutectic points lie on the common freezing point of component *A* (3).

Department of Physical Chemistry, University of Warsaw

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
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CHEMISTRY

Binary Solid Solutions and Eutectic Mixtures Formed by One Component with Representatives of a Series of Homologues

by

T. PENKALA

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of January 12, 1953

Some time ago W. Świętosławski [1] published a paper in which he suggested that the examination of binary mixtures formed by substance A with representatives of a series of homologues, B, B_1, $B_2 \ldots B_n$, showed a gradual transition from ideal eutectics (pure components in solid phases), through eutectics of solid solutions, to solid solutions characterised by unlimited mutual solubility (Fig. 1).

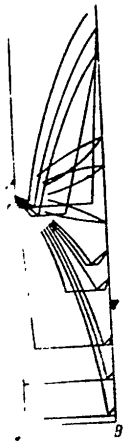

Fig. 1

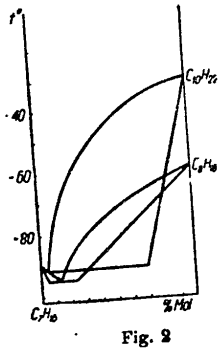

Fig. 2

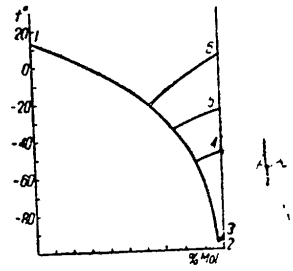

Fig. 3

Fig. 1. Gradual transition from eutectics to solid solutions according to the scheme given by Świętosławski. The upper part of the diagram is extended to cases in which the higher melting representatives of the series form eutectics with component A

Fig. 2. Eutectics formed by *n*-heptane

Fig. 3. Eutectics formed by *n*-decane

Świętosławski's suggestion is now confirmed and extended. A gradual transition really occurs in the series of paraffins and depends on the differences in length of the carbon atom chains.

The extension of the diagram given in 1949 by Świętosławski consists in the addition of the upper part, in which component A, characterised by relatively low melting point t_A, forms eutectics with the representatives with considerably higher melting points.

In Figs. 2 and 3 all the combinations formed by n-heptane, n-octane and n-decane are shown. In addition the diagram shown in Fig. 4 demon-

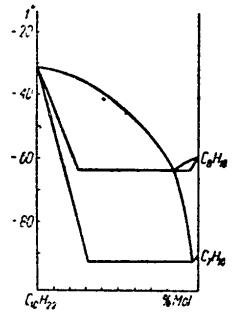

Fig 4. Eutectics formed by n-octane with three other paraffins. $C_{32}H_{66}$ forms an ideal eutectic, the two other non-ideal ones

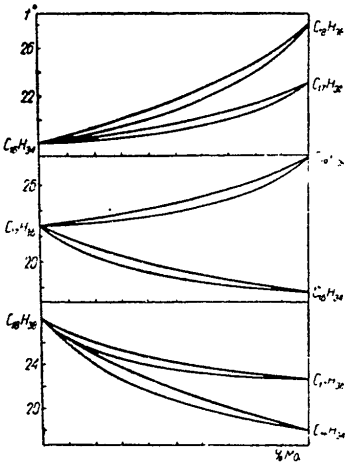

Fig. 5. A series of solid solutions formed by paraffins

strates that the eutectic points lie on one curve independently of whether the solid phases are pure components or solid solutions.

Seyer [3] showed that the systems formed by (C_4H_{10}, $C_{32}H_{66}$), (C_6H_{14}, $C_{32}H_{66}$), (C_8H_{18}, $C_{32}H_{66}$), ($C_{16}H_{34}$, $C_{32}H_{66}$) and ($C_{20}H_{42}$, $C_{32}H_{66}$) are eutectics due to the large differences in the length of the chains.

The same phenomena take place in other binary mixtures if, for instance, substance A does not belong to the same series of homologues.

Chlorobenzene, bromobenzene and iodobenzene form with each other solid solutions characterised by their unlimited solubility; with fluorobenzene, however, systems with limited solubility appear. This is associated with a considerable difference in the size of the atoms involved.

Similar phenomena are observed in many other cases and discussed in a paper to be published shortly in "Roczniki Chemii". In all these cases a gradual transition takes place from solid solutions with unlimited solubility torugh those characterised by a limited solubility to ideal eutectics.

Department of Physical Chemistry, University of Warsaw

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BULLETIN DE L'ACADÉMIE
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CHEMISTRY

Coal Tar as a Typical Polyazeotropic Mixture I

by

W. ŚWIĘTOSŁAWSKI

Communicated at the meeting of January 12, 1953

1 Polyazeotropic Systems. Three kinds of polyazeotropic systems have been examined. In previous papers [1] we use the term "positive polyazeotrope" for designating a system in which agents A, B and C, both separately and in combinations of two or three, can form with a series (H) of homologues, their isomers or other closely related substances, positive azeotropes of the general types (A, H_l), (A, B, H_l) and (A, B, C, H_l).

If a weak acid (A) forms with a homologous series of weak bases (P) a number of negative azeotropes $[^{(-)}A,P_l]$, or if a weak base (P) forms with a series of weak acids (A) a similar series of negative azeotropes $[^{(-)}P,A_l]$, we call them negative polyazeotropic systems [2].

Finally, any negative azeotrope $[^{(-)}A,P]$ may form with a series of homologues and their isomers (H) a positive-negative polyazeotropic system $[^{(-)}A,P\ ^{(-)}H_l]$ [3]. Quaternary positive-negative azeotropes of the general type $[^{(-)}A,P^{(-)}B\ H_l]$ are as yet unknown; their existence, however, is very probable [4].

2 Polyazeotropic Mixtures. Mixtures of two or more polyazeotropic systems will be referred to as polyazeotropic. According to this nomenclature, low and high temperature coal tar, petroleum, synthetic liquid fuels and similar liquids should be regarded as polyazeotropic mixtures. It should be emphasized that the number of components forming polyazeotropic mixtures and their concentrations may vary to a very large extent in different liquid mixtures. Of these numerous polyazeotropic mixtures, coal tar is the most complicated because of the number of homologous series, the constituents of which each play their part in the formation of different kinds of azeotropes.

3 Main Component of a Polyazeotropic Mixture. For a proper understanding of the complicated phenomena taking place in the course of a batch distillation of different oils separated from coal tar, it is important to find out whether or not in the oil being distilled there exists

a substance in sufficient quantity to form with other constituents all t azeotropes which might be formed under a certain pressure established the distillation still. This substance will be called, both in this and in other papers of this series, the **main component** of the polyazeotr mixture.

In a middle oil, naphthalene is the main component, because it is pres in such a quantity, that at the end of the distillation, besides the azeotro formed by it, its excess appears as a "zeotropic component" in the fracti collected. At the final moment of the distillation, the distilling curve rea the horizontal line corresponding to the boiling temperature of pure n thalene: 218.2° C. Some time later fractions are collected at successively creasing temperatures. From then on almost tangent zeotropes [5] of naph thalene with higher boiling constituents of the mixture are collected in th receiver.

In Fig. 1 is shown a typical distilling curve obtained for a middle oi

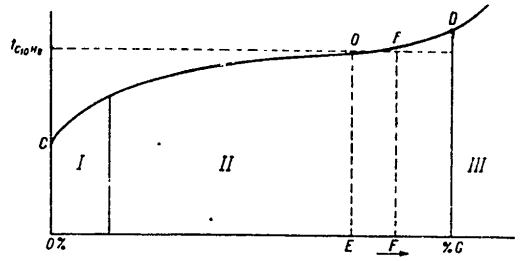

Fig. 1. Distilling curve obtained for a batch distillation of a middle oil. Part II corresponds to that fraction in which numerous azeotropes formed by naphthalene with other constituents are collected in the receiver

Similar shapes of distilling curves may be obtained for other polyazeotropic mixtures, in which the main component is present.

The horizontal line drawn through a point representing the boiling temperature of the main component is called the **azeotropic ceiling line**.

If a large excess of the main component is present, some fraction of the distilling curve merges with the azeotropic ceiling line. On the other hand, a large number of high boiling constituents of the mixture exert their influence on the composition of the distillate. For this reason the distilling curve may cross the ceiling line at an acute angle. This case is shown in Fig. 1. Such a phenomenon occurs when a middle oil is submitted to a fractional batch distillation. Higher boiling isomeric methylnaphthalenes are responsible for the absence of that section of the distillation curve which merges with the azeotropic ceiling line.

4 Polycomponent Azeotropic Agent for Naphthalene Removal. The mother liquor, obtained after the naphthalene crystals have been removed by any one of the known procedures, represents a typical mixture of substances which, taken together, may be considered as a polycomponent azeotropic agent for the azeotropic removal of naphthalene from any oil containing this substance.

Extensive research and numerous experiments carried out by a group of Polish researchers on laboratory, pilot-plant and industrial distilling installations have proved that the recycling of a polycomponent azeotropic agent favours its self-improvement. In fact, in each cycle the azeotropically inactive constituents are automatically removed from the main fraction in the course of distillation. They are found either in the forerunnings or in higher boiling fraction and bottom product, respectively.

5. Final Remarks. The example in which naphthalene is the main component should be considered as a typical one for any polyazeotropic mixture. In other batch distillations similar phenomena can be observed in all those cases in which the main component is present. Some of these cases will be described in other papers of this series.

SUMMARY

1. Definitions of the terms: polyazeotropic system, polyazeotropic mixture, main component, azeotropic ceiling line and polycomponent azeotropic agent are given.

2. Low and high temperature coal tar, petroleum, synthetic fuels etc. are considered as polyazeotropic mixtures. It has been emphasized that coal tar is the most complicated polyazeotropic mixture yet examined.

3. The distillation of a middle oil has been used as a typical example of the way in which naphthalene forms numerous azeotropes with other tar constituents and plays the role of the main agent.

4. The mother liquor obtained after the removal of naphthalene crystals has been found the most suitable polycomponent agent for azeotropic removal of naphthalene from tar oils.

5. The recycling of the polycomponent azeotropic agent favours the removal of constituents which are unable to form azeotropes with the main component. In that way, in the course of recycling, a self-improvement of the azeotropic agent takes place.

6. The phenomena found when naphthalene is the main component resemble those which are typical of other polycomponent mixtures.

Department of Chemistry, University of Warsaw

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BULLETIN DE L'ACADÉMIE
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CHEMISTRY

On the Positive-Negative Azeotropes Formed by Naphthalene, Cresols and Pyridine Bases. XIX

by

K. ZIĘBORAK and H. MARKOWSKA-MAJEWSKA

Presented by W. ŚWIĘTOSŁAWSKI on March 29, 1954

Introductory remarks

The purpose of these investigations was to examine by the ebulliometric method [3], [4] three systems composed, on the one hand, of naphthalene and a cresol fraction F, boiling at practically constant temperature 202° C., and on the other, of three fractions of pyridine bases P_1, P_2 and P_3, each used separately.

The boiling temperature ranges of the three fractions were: P_1: 142—145° C.; P_2: 157—157.5° C. and P_3: 163—164° C. Experiments have shown that the isobars obtained by mixing each of the base fractions separately with a cresol fraction F, are each characterized by a maximum boiling temperature. The maxima corresponded to mixtures behaving as if each of them consisted of only a binary negative azeotrope.

Experimental part

In Table I are listed: the composition, the boiling temperatures and the increases in azeotropic boiling temperature.

TABLE I

Maximum boiling temperature of mixtures $[(-)F, P_1]$, $[(-)F, P_2]$, $[(-)F, P_3]$

Mixture	Weight percent of P at maximum	Maximum boiling temp. $t_{(-)F,P}$	Azeotropic temp increase $t_{(-)F,P} - t_F$
$F + P_1$	10%	202.5	+0.5
$F + P_2$	20%	204.4	+2.4
$F + P_3$	22%	204.9	+2.5

In Fig. 1 points C_1, C_2 and C_3 correspond to the compositions of mixtures $[(-)F, P_1]$, $[(-)F, P_2]$ and $[(-)F, P_3]$, each being characterized by a maximum boiling temperature.

Table II contains the figures obtained from an ebulliometric examination of the boiling temperature isobars formed by naphthalene (H) together with the mixtures C_1, C_2 and C_3. In columns II, III and IV of Table II are listed the weight percentages of naphthalene at the minimum boiling temperatures M_1, M_2 and M_3 and the decreases in boiling temperatures, when compared with $t_{(-)F,P_1}$ found for mixtures represented in Fig 1 by points C_1, C_2 and C_3.

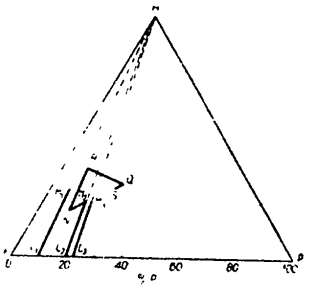


Fig 1 Projection on the concentration triangle of the maximum boiling points C_1, C_2, C_3 and the minimum ones M_1, M_2, M_3 of mixtures of (F, P_1, H) (F, P_2, H) and (F, P_3, H), where H stands for naphthalene. Points C_1, M, N, R, Q and S correspond to the various compositions of mixtures. The thick straight lines are the projections of isobars examined by the ebulliometric method

TABLE II

Minimum boiling temperatures of naphtalene mixed with (F, P_1), (F, P_2) and (F, P_3)

I	II	III	IV
$F, P_1 + H$	10	202.48	− 0.02
$F, P_2 + H$	18	204.03	− 0.37
$F, P_3 + H$	21	202.39	− 0.51

In addition to examination of the shape of the boiling temperature isobars, the corresponding sections [1] HC_1, HC_2 and HC_3 of the main lines are graphically represented in Fig. 1 by thick lines. Other isobars were examined for the purpose of determining the position of the azeotropic points. For instance, lines MN, NR, RQ and QS represent the isobars examined for mixtures composed of H, F and P_2 (Fig. 1).

Discussion of the results

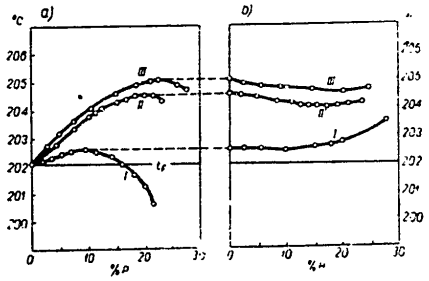
The conclusions drawn from these experiments may be formulated as follows:

1. All of the ternary positive-negative azeotropes [2] formed by naphthalene, meta and para-cresols and the picolines and lutidines found in the three fractions P_1, P_2 and P_3 belong to the almost tangent type.

2. The tridimensional surfaces of the isobars of all these azeotropes, and also of their mixtures are very flat near points C_1, C_2 and C_3.

3. Points t_{A_2}, which correspond to the compositions of the ternary saddle-azeotropes under consideration, and also all the three top-ridge lines lie inside triangle HCP.

4. The boiling temperatures of all the azeotropes involved differ so little from each other that their separation by an effective distilling column seems to be impossible.



Figs. 2a and 2b. Curves I, II, III represent the boiling temperature isobars of mixtures of a cresol fraction F with each of the three pyridine bases. I′, II′, III′ are the corresponding isobars formed by mixtures of F, P_1, F, P_2. F, P_3 with naphthalene

In order to prove these conclusions, a mixture of naphthalene (17.5%), a fraction of meta and para-cresols (62.5%) and a fraction P_1 (142 - 145° C.)

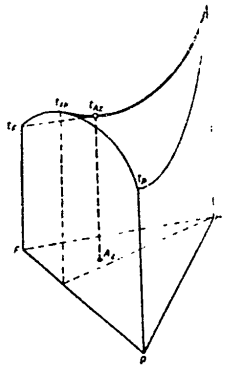


Fig. 3. Tridimensional model of a saddle azeotrope composed of naphthalene (H), one of the cresols (F) (meta or para) and one of the constituents of pyridine bases fraction P_2. Point t_{Az} represents the boiling temperature of this azeotrope This point is situated on the top-ridge line, which lies in the vicinity of the main line [2]

of pyridine bases (20.0%) was submitted to fractional distillation on a thirty-five plate column. The main fraction, corresponding to 75% of the charge, was collected within 202.5—203.7° C., and the average contents of these mixtures were found for tar bases 10.4%, for naphthalene 20.6% and for

cresols 69.0%. It should be noted, that fraction P_1 used in this experiment was characterized by the largest boiling-range of temperature, 142—145° C., compared with the two others, P_2 and P_3. For comparison, in Figs. 2 a and 2 b, two series of boiling temperature isobars I, II, III and I', II', III', are given. A corresponding explanation is given in the legend of the two drawings.

One should note that curve I' is almost tangent to the horizontal line drawn through point t_M, and that the two other isobars are slightly concave, showing relatively small depression of the boiling temperatures.

This is certainly in agreement with the figures listed in the last column of Table II.

A tridimensional model of a ternary saddle azeotrope [(—) F, P (+) H] is shown in Fig. 3. The system is composed of naphthalene, one of the cresols (meta or para-isomer) and one of the components of fraction P_2.

We wish to express our thanks to Prof. Świętosławski for his help and advice.

Summary

1. The ebulliometric method was used for determining the shape of the boiling temperature isobars of systems composed, on the one hand, of naphthalene and a fraction F of m and p-cresols, characterized by the constant boiling temperature, $t_F = 202°$ C., and, on the other, of fractions of pyridine bases characterized by the following temperature ranges: P_1: 142—145° C., P_2: 157—157.5° C., P_3: 163—164° C.

2. It was found that all three isobars were characterized by minimum boiling temperatures, indicating that each of the mixtures was composed of a corresponding number of three-component positive-negative (saddle) azeotropes characterized by boiling temperatures differing very little from one another.

3. The boiling temperatures of the three mixtures of positive-negative azeotropes formed by naphthalene, with a fraction F of m and p-cresols, and of the three pyridine bases P_1, P_2 and P_3 differed slightly from the maximum boiling temperatures formed by fraction F mixed with P_1, P_2 or P_3 respectively.

4. The tridimensional surface corresponding to the boiling temperature isobars was examined by the ebulliometric method, and it was found that in the vicinity of the minimum boiling temperature lying on the top-ridge line [2], these surfaces were very flat. Therefore, it may be said that the behaviour of each of the three above-mentioned polyazeotropic mixtures was similar to that of a single ternary saddle azeotrope composed of three individual substances.

5. The formation of a polyazeotropic mixture consisting of a number of ternary saddle azeotropes [(—) F, P (+) N], F, P and N representing one of the cresols, one of the pyridine bases and naphthalene respectively, takes place in the course of distillation of the carbolic and middle oils of coal tar.

Institute of General Chemistry, Warsaw

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CHEMISTRY

Polyazeotropic Mixtures Containing Two or More Series of Homologues. II

by

W. ŚWIĘTOSŁAWSKI

Communicated at the meeting of December 13, 1954

1. Classification of Polyazeotropic Mixtures

In the preceding paper of this series [1] coal tar and tar oils were called polyazeotropic mixtures. In this paper an attempt is made to classify the polyazeotropic mixtures more precisely. Namely, if a liquid organic raw material or any product obtained by its fractional distillation contains two series of homologues and their isomers, for instance, if one is composed of paraffins (H), the other of aromatics (Ar), it is reasonable to call it a two-series polyazeotropic mixture. Consequently, for liquids containing three or more series of homologues and their isomers, the term polyazeotropic mixture should be supplemented by the number of the series of homologues and their isomers which are the constituents of that mixture.

Coal tar or at least some tar oils contain not less than six series of homologues, namely: (H), (Ar_1), (Ar_2), (F), (P), (Am). The symbols represent: (H) — paraffins, (Ar_1) — one-ring aromatics, (Ar_2) — two-ring aromatics, (F) — phenols, (P) — pyridine bases, (Am) — aromatic amines. We purposely omit the series of olefines (O) and the naphthenes (N), because they are found in high temperature coal tar in small quantities and, in addition, their azeotropic ranges [2] differ little in respect to the paraffins and aromatics so that they do not exert any notable influence on the course of distillation. In low temperature coal tar, however, the concentrations of olefines are considerably larger and their influence on distillation cannot be neglected.

2. Polyazeotropic Mixtures Composed of Two Series of Homologues

Let us suppose, for simplification, that large quantities of two mixtures (H) and (Ar) have been prepared by mixing equal molar quantities of each of the representatives of series (H) on the one hand and of series (Ar)

on the other. Using these two mixtures we would be able, for instance, to prepare the following three polyazeotropic mixtures in which m changes from 19 to 1:

Number	Weight % of H	Weight % of Ar	$C_{H_l} = mC_{Ar_j}$	m
1	95%	5%	$C_{H_l} = 19C_{Ar_j}$	19
2	75%	25%	$C_{H_l} = 3C_{Ar_j}$	3
3	50%	50%	$C_{H_l} = C_{Ar_j}$	1

Suppose that the azeotropic ranges [2] of all the components of series (Ar) are known; for instance, for Ar_j we may write.

$$Z_{Ar_j}(H) = t_{H_k} - T_{H_e},$$

where H_k and H_e are the representatives which form with Ar_j two tangent azeotropes [3]. Suppose also that the boiling temperatures t_{H_l} and t_{Ar_j} are equal or almost equal to each other.

Let us consider the phenomena which would take place if the three mixtures mentioned above were submitted to a fractional distillation. Because of the small amounts of each of the members of series (Ar) in mixture 1 the component Ar_j would form successively an almost tangent zeotropic isobar with the representative H_{e-1}, a tangent one with H_e and an almost tangent azeotropic isobar with H_{e+1}. When distilling mixture 2, we would observe that the corresponding azeotropes (Ar_j, H_{e-2}), (Ar_j, H_{e+2}) would be formed. Finally, if a mixture of equal concentrations of the representatives of both series were submitted to fractional distillation, curve III shown in Fig. 1 *c* would represent graphically the large increase in concentration of the component Ar_j.

We have examined the case in which the differences in boiling temperatures of components $t_{H_{e-1}}, t_{H_e}, t_{H_{e+1}}$ and $t_{Ar_{j-1}}, t_{Ar_j}, t_{Ar_{j+1}}$ were so large that no superimposing of concentration curves took place. If these differences were smaller, azeotropes formed by Ar_{j-1} and Ar_{j+1} would be admixed to those formed by the component Ar_j. These phenomena are frequently encountered in cases of industrial batch distillations of different polyazeotropic mixtures.

Let us, however, return to our simplified case and formulate some of the phenomena taking place when a two-series polyazeotropic mixture is submitted to fractional distillation. First, if the molar concentrations of each representative of series (Ar) are smaller than those of the components of series (H), such a polyazeotropic system may be called a two series (H) polyazeotropic mixture. Symbol (H) denotes the preponderance of concentrations of components (H) as compared with those of (Ar). In this case any substance Ar_j undergoes distillation within a narrow range of tempe-

ratures close to the lowest one, t_{H_e}, at which Ar_j forms with H_e a tangent isobar with respect to the horizontal line drawn through point t_{H_e}. With an increase of the molar concentration of Ar_j, there is a corresponding increase in the number of azeotropes formed with the representatives of series (H). Secondly, if the concentrations of any of the components of both the (H) and (Ar) series, for instance, H_l and Ar_j, boiling practically at the same temperatures, become equal $(m=1)$, the preponderance of concentrations of the components of any of these series disappears. In that case the largest amount of azeotrope (Ar_j, H_l) is found in the receiver. At the moment of maximum concentration of Ar_j in the distillate the condensation temperature is close to 0.5 $(t_{Ar_j} - t_{H_e})$. Similar phenomena take place, if the polyazeotropic mixture is prepared so that the components of the series (Ar) are in larger concentrations than those belonging to series (H). In the latter case curves *I*, *II* and *III* refer to component H_l and not to Ar_j.

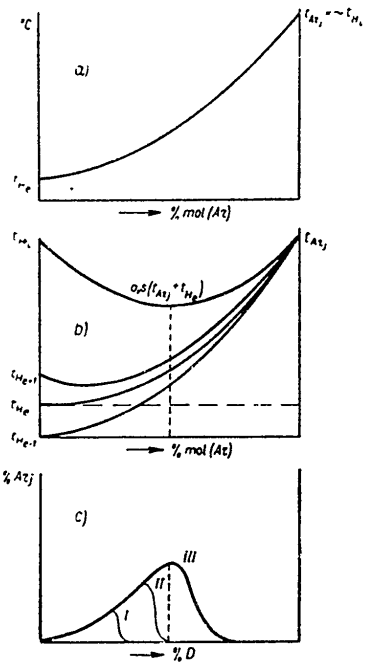

Fig 1. A section of the distilling curve is represented in scheme *a*. It starts with condensation temperature t_{H_e} and ends with t_{Ar_j}. Scheme *b* shows the shape of several boiling temperature isobars starting with the almost tangent "zeotropic" one, $t_{H_{e-1}} t_{Ar_j}$, and ending with $t_{H_{e+1}} t_{Ar_j}$, which is characterized by a relatively small depression Δt. In scheme *c* curves *I*, *II* and *III* correspond to the changes in concentrations of Ar_j in the distillates, when mixtures 1, 2 and 3 are submitted to fractional distillation

When dealing with industrial products, we have to take into consideration the fact that they are more complicated polyazeotropic mixtures than those mentioned above. Some similarity, however, may be noticed if we examine the distillation of low, medium and high boiling gasolines. In the case of low boiling gasoline, benzene and then toluene start to appear in the receiver at lower temperatures than their own. The larger the lower portion of the azeotropic range [2] of Ar_j, the lower is the boiling temperature of the mixture containing a small amount of the corresponding aromatic hydrocarbon. It is a well-known fact that benzene and toluene

may be easily entrained by nonaromatic hydrocarbons which form with benzene or toluene tangent zeotropes and azeotropes before the next aromatic hydrocarbon starts to appear at the top of the distilling column. On the other hand, the xylene isomers boil so close to one another that curves *I*, *II* and *III* shown in Fig. 1c become superimposed one on top of the other.

For the sake of simplicity we do not mention that gasoline contains naphthenes as the third series of homologues. They do not produce any notable influence on the shape of the distilling curve. They form azeotropes with aromatic hydrocarbons (Ar_j, N_l), which behave in a similar way to those composed of H_l instead of N_l, where symbol N stands for any representative of the naphthene series.

3. Methods for Studying More Complicated Polyazeotropic Mixtures

Much more complicated phenomena take place if more than two series of homologues are present in a polyazeotropic mixture. Beside low- and high temperature coal tar and different tar oils, other industrially important liquids belong to this type of polyazeotropic mixture. A special technique based often on fractional distillation and on ebulliometric investigation of closely boiling fractions collected in the course of a batch distillation carried out on a pilot plant or industrial column, has to be applied in order to obtain more information concerning the phenomena associated with both an azeotropic and a zeotropic distillation of these mixtures. By removing phenols, organic bases, olefines, etc. it becomes possible to reduce the number of homologous series. In that way a direct comparison of the distillation curves obtained before and after the reduction of the number of homologous series, offers important information concerning the influence exerted by one, two or sometimes three series of homologues and their isomers [3].

In some particular cases certain components may be removed by crystallization and the shape of the distilling curves before and after the removal of those components may also be directly compared [3], [4].

Another method consists in adding a large excess of a certain component so as to produce all the azeotropes formed by it. The result of this procedure is often important for understanding some phenomena taking place during the distillation [5].

A group of Polish scientists are at present engaged in carrying out experiments in order to find the most suitable conditions for studying different polyazeotropic mixtures.

Summary

1. The polyazeotropic mixtures have been classified according to the number of homologous series contained in them.

2. In order to examine the most typical phenomena taking place in the course of a batch distillation, it was assumed that two liquid systems had been prepared, one (H) containing equimolecular quantities of representatives of one homologous series, another

by equimolecular quantities of the other series. Afterwards, typical mixtures were prepared by mixing these two systems so as to obtain mixtures with varying ratios $\sum_i C_{Ar_j} = m$.

3. If ratio m is large enough, each of the representatives of series (Ar_j) is collected in the receiver at temperatures differing slightly from t_{H_e} of the component H_e, which forms with Ar_j a tangent azeotrope.

4. For studying the distillation phenomena taking place during the batch distillation of a polyazeotropic mixture, the distillation and ebulliometric methods are combined with the removal of acid, basic and neutral components. Sometimes a certain component is removed by crystallization. In other cases a large amount of an agent is added, which is able to entrain azeotropically a large number of components belonging to one, two, sometimes three series of homologues.

Department of Physical Chemistry, University of Warsaw

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CHEMISTRY

Cryometric investigation of fractions obtained by fractional distillation of 2-pilcoline

by

W. ŚWIĘTOSŁAWSKI and R. CIECHOMSKA

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of December 13, 1954

1. Introductory remarks

Some years ago Coulson and Jones [1] described the phenomena taking place when pyridine bases are submitted to a fractional distillation on an effective distilling column. Under these conditions relatively large intermediate fractions are obtained without any sharp transition separating the pyridine, 2-picoline and so-called three-degree fraction 142-145°C. levels on the distilling curve. On the other hand, W. Głowacki [2] determined the most important physical properties of a pure 2-picoline sample, but made no mention of the difficulties to be encountered in preparing the pure base under consideration. For this reason it seemed important to examine, by means of the cryometric method, the fractions collected in the course of a fractional distillation of a 2-picoline fraction obtained from a technical product on a large-scale batch distilling column.

2. Cryometric examination of pyridine bases

It was shown in previous papers [3], [4], [5] that a suitable method for examining pyridine bases and their mixtures consists in a cryometric examination of dehydrated hydrochlorides.

A sample of the pyridine base is treated with hydrochloric acid and brought to the boil, and then the excess of hydrochloric acid is easily removed with water vapour. The hydrochloride salts of all the pyridine bases boil at temperatures exceeding 200°C. Because of that, there is no difficulty in proving that the removal of water and hydrogen chloride is a quantitative one. Experiments [3] have shown, however, that the samples of any of the hydrochlorides thus obtained contain an excess of hydrogen chloride. This is the only disadvantage of the method, because, owing to this excess, the freezing temperature of the melted hydrochloride decreases with an increase in the amount of the solid phase.

In our experiments we determined three equilibrium temperatures: t_1, $t_{1/2}$ and t_2, where t_1 is the temperature at which the last crystals disappear, t_2 – that at which from 80 to 90% of the hydrochloride becomes solidified, and $t_{1/2}$ corresponds to a state in which one half of the sample is in the solid and the other half in the liquid phase. For simplification, only t_1, the temperature at which the crystals disappear, will be considered in this paper.

3. Cryometric measurements of forerunnings: main and end-fractions

It should be emphasized that technically pure 2-picoline fractions usually contain appreciable amounts of pyridine, 3-picoline, 4-picoline and 2,6-lutidine. Among these bases 2-picoline is characterized by the lowest value of t_1. Below t_1 the values are given for all of the pyridine bases mentioned above.

Hydrochlorides	t_1°C	3-Picoline	85
Pyridine	137.5	4-Picoline	161
2-Picoline	78	2,6-Lutidine	238

Because of the large difference in the freezing temperatures of pyridine and 2,6-lutidine, the former precipitates in the forerunnings and the latter in the end fractions of the batch distillation of technically pure 2-picoline. For this reason, when experimenting with the hydrochlorides, we must bear in mind that the above-mentioned contaminants should be called "main components" in the fractions collected at the beginning and at the end of the distillation. This is due also to the fact that the pyridine base hydrochlorides form eutectics with one another.

On the other hand, the middle fractions after being transformed into hydrochlorides, contain such an excess of 2-picoline that the precipitating crystals of the melted hydrochloride salts contain practically pure 2-picoline hydrochloride.

On the basis of the facts mentioned above, it is easy to conclude that in the forerunnings as well as in the end fractions two samples have to be found which, after being transformed into hydrochlorides, should each be characterized by a certain minimum "freezing" temperature.

The composition of these two samples should correspond or approximate closely to the composition of the two eutectics. The first minimum indicates that the composition of the sample is very similar to that of the eutectic pyridine- 2-picoline hydrochlorides, and the second that of the eutectic of 2-picoline- 2,6-lutidine hydrochloric salts. Thus the two fractions showing the minimum freezing temperatures of the hydrochlorides divide the distillation curve into three sections. In the first of these, pyridine hydrochloride is the main component, in the second, 2-picoline hydrochloride, and in the third, 2,6-lutidine. Consequently, when preparing a pure 2-picoline sample, the middle fraction

only should be used for further recrystallization of the hydrochloric salt from the free base.

It should be pointed out that similar phenomena can be observed in all cases in which an intermediate fraction separates the two others which correspond to two chemically pure compounds collected in the receiver. These two substances should form with each other an ideal binary eutectic.

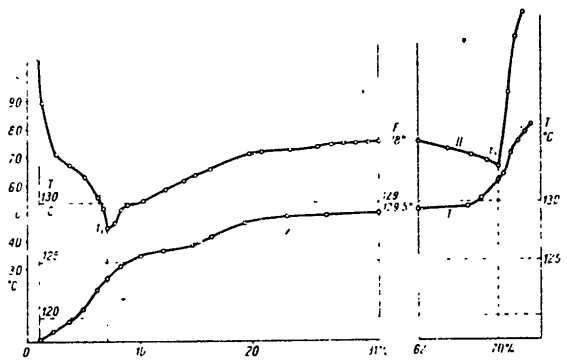

Fig. 1. Distillation curve *I* of a technically pure 2-picoline fraction. Curve *II* shows the temperature changes, corresponding to the disappearance of crystals in the melted hydrochloric salts. Temperatures t_1 and t'_1 correspond to the two minimum freezing" temperatures indicating the existence of two eutectics: pyridine-2-picoline and 2-picoline-2,6-lutidine hydrochlorides, respectively. The main fraction *F* was collected within 129.0-129.5°C. Its "freezing" temperature was constant and equal to 78°C. Fraction *F* was collected within limits ranging from 31 to 62%. This part of the drawing was omitted in order to shorten the length of the figure.

It was stressed above that the temperature of the disappearance of crystals and not the "freezing" temperature was measured in our experiments. This was due to the supercooling phenomena which often take place not only in the case of pyridine base hydrochlorides, but in many other cases as well.

The physical properties of the fraction of 2-picoline collected within 129.0-129.5°C. did not differ from those described by Głowacki [2].

Summary

1. A batch distillation of a technically pure 2-picoline may be combined with a cryometric investigation of the fractions after their transformation into hydrochlorides. The removal of water and hydrochloric acid is an easy operation.

2. The curve showing the change in temperature at which the disapperance of crystals in the melted hydrochloride takes place is composed of three sections. In the

first, pyridine hydrochloride is the main component; in the second, 2-picoline hydrochloride precipitates first; in the third, 2,6-lutidine salt is the main component of crystallization. The three sections are divided from each other by hydrochlorides which show minima t_1 and t_1' corresponding to the disappearance of crystals. These minima show the formation of two binary eutectics. The first (t_1) corresponds to the eutectic pyridine- 2-picoline hydrochloride, the second (t_1') to the system: 2-picoline- 2,6-lutidine hydrochlorides.

3. There is no evidence that pyrol is present in the technical 2-picoline fraction used in this investigation.

DEPARTMENT OF PHYSICAL CHEMISTRY UNIVERSITY OF WARSAW

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CHEMISTRY

On the azeotropic range of acetic acid with respect to the homologous series of paraffin hydrocarbons

by
Z. KURTYKA

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of December 13, 1954

1. Introductory remarks

A method for determining the azeotropic ranges of a certain agent A with respect to hydrocarbons has been described by W. Świętosławski and A. Orszagh [1]. This method consists in using some fractions of gasoline, boiling within such a temperature range as to have the lowest H^e and the highest H_k representatives forming with agent A tangent, or almost tangent, boiling temperature isobars. It is not possible with this method to determine the shape of the isobars formed by A with each of the representatives of series (H).

Having in view the determination of one point only on the isobar, corresponding to the boiling temperature and to the composition of each individual azeotrope, a large majority of investigators have used exclusively the fractional distillation method [2]—[6].

In the present investigation acetic acid was chosen as the azeotropic agent because of the large azeotropic range of this substance with respect to normal paraffins. The purpose of these investigations was to determine, by means of the ebulliometric method, the composition of the azeotropes and also the shape of the boiling temperature isobars formed by the acetic acid with each of the normal paraffin hydrocarbons.

Further details concerning this investigation as well as those relating to purification, analysis and the technique of the ebulliometric measurements will be described elsewhere [7]. It must be stressed that care was taken to operate with highly dehydrated substances and their mixtures.

2. Ebulliometric method of measurements

The ebulliometric method consists in observing the changes both in the boiling and in the condensation temperatures each time a known

quantity of one of the components is added. Two Swietoslawski ebulliometers were used for this purpose. A simple one filled with water served for measuring the pressure changes and a differential one, composed of three sections, was used for determining the boiling temperature and also the two condensation temperatures of the liquid vapour system under examination. The results obtained are listed in Table I. In column I are listed the boiling temperatures of the various azeotropes examined, in column II – the composition of each azeotropic mixture expressed in weight percentage of A (%G), and in column III the azeotropic depressions calculated with respect to the lower boiling component.

TABLE I

Substances	I	II	III
Acetic acid A — (118.05)	—	—	
„ „ -n-hexane (68.60)	68.25	6.0	0.35
„ „ -n-heptane (98.25)	91.72	33.0	6.53
„ „ -n-octane (125.30)	105.70	53.0	12.35
„ „ -n-nonane (150.20)	112.80	69.0	5.25
„ „ -n-decane (173.30)	116.75	79.5	1.30
„ „ -n-undecane (193.85)	117.72	95.0	0.33

It can be seen that the shapes of the corresponding isobars are very flat, especially in the vicinity of the azeotropic points. With an increase in the boiling temperature of the homologue, the flat shape of the isobars becomes more distinctly pronounced and approaches that of the isobars characteristic for typical binary heteroazeotropes. This may be illustrated by the following example: the mixtures of acetic acid and n-nonane, containing from 22.5 to 41 weight per cent of nonane, boil within the narrow range of temperature of 0.15° C.

In addition, it should be noted that the sections of the isobars lying near the corresponding azeotropic points are asymmetrical.

The flat shape of all the isobars examined is probably due, to some extent at least, to the restricted mutual solubility of the components. At room temperature the mixtures formed by normal paraffins (ranging from n-hexane to n-octane) with acetic acid are homogeneous, whereas the higher boiling paraffins form with acetic acid two liquid phase systems.

The azeotropic range of acetic acid is very large:

$$Z_A(H) = t_{H_k} - t_{H_e} = 193.85 - 68.6 = 125.25°C.$$

in this equation t_{H_k} and t_{H_e} are the respective boiling temperatures of n-undecane, U, and n-hexane, H_e; it should be stressed that both these hydrocarbons form almost tangent "azeotropic" isobars.

The boiling temperatures of the two azeotropes are

$$t_{(Ac,U)} \quad t_{Ac} \quad 0.33^0\,C$$

$$t_{(Ac,H_e)} \quad t_{H_e} \quad 0.35^0\,C.$$

t_{Ac}, $t_{(Ac,U)}$ and $t_{(Ac,H_e)}$ being the normal boiling temperatures of acetic acid and of the two azeotropes formed by acetic acid with *n*-undecane

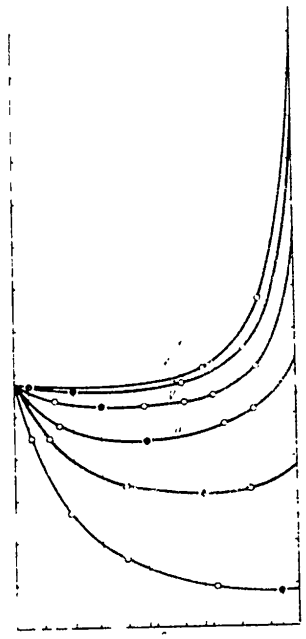

Fig. 1. Boiling temperature isobars formed by acetic acid *A* with paraffin hydrocarbons (*H*). Curves from I to VI represent the isobars formed by acetic acid with paraffins ranging from *n*-hexane (I) to *n*-undecane (VI). Because of lack of space, several points only are given on curves V and VI, instead of the large number of points established experimentally

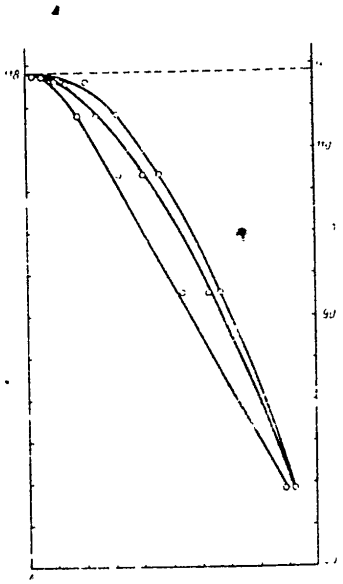

Fig. 2. Curves I to III represent the relation between the boiling temperatures of azeotropic mixtures as a function of the composition of *A* in weight (I), mole (II) and volume (III) percentages

or *n*-hexane. The neighbouring representatives: the lower boiling *n*-pentane and the higher boiling *n*-dodecane form with acetic acid typical "zeotropic mixtures".

To get tangent isobars for mixtures of Ac and U and of Ac and H_e, the pressure under which the isobar has to be examined should be changed correspondingly.

It may be seen below that the azeotropic range $Z_A(H)$ is characterized by a large degree of asymmetry. In fact, in its lower portion $t_{Ac}-t_{H_e}$ is equal to 49.5° C. and in its upper one $t_U-t_{Ac}=75.8°$ C.

As to the shapes of the isobars shown in Fig. 1 they are asymmetrical with respect to their azeotropic points. This indicates that the fractional distillation method of preparing azeotropes may give rise to errors. In fact, the flat and asymmetrical character of the isobars does not favour a sharp separation of the fraction representing the exact composition of the azeotrope obtained by distillation. For this reason, in determining the exact composition and the boiling temperatures of azeotropes formed by acetic acid with hydrocarbons, the ebulliometric method offers better results than the distillation method.

In Figure 2 the shape of curve II representing the relation between changes in the azeotropic temperatures of the respective mixtures as a function of composition (mols per cent) cannot be presented by using an empirical equation similar to those suggested by H. Skolnik [8] for other azeotropes. In this case better results might have been obtained if an equation similar to that used by Lecat [9] had been applied.

I wish to express my thanks to Professor W. Świętosławski for his help and advice.

Summary

1. The boiling temperature isobars formed by mixtures of acetic acid with normal paraffins, ranging from *n*-hexane to *n*-undecane, were ebulliometrically examined. The boiling temperature and the composition of each azeotrope are listed in Table 1.

2. Experiments have shown that the isobars are characterized by very flat sections in the vicinity of the azeotropic points.

3. Normal hexane is the lowest and normal undecane the highest boiling paraffin forming almost tangent "azeotropic" isobars with acetic acid.

4. All the isobars are characterized by asymmetry of the sections lying near the point representing the composition of the azeotropic points.

5. The lower portion of the azeotropic range is much smaller (45°C.) than the upper one (75°C.).

DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF WARSAW

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CHEMISTRY

Ideal eutectic systems

by

W. MALESIŃSKI

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of December 13, 1954

1. General assumptions

Let us consider a series of two- three- or multicomponent systems formed by any organic compounds which do not react with each other and do not form intermolecular complexes. Let them form so-called simple eutectic systems in which the liquid homogeneous phase is in equilibrium with the solid phases, each solid phase consisting of a pure component.

In order to determine the equilibrium temperatures in the whole concentration range it is necessary to know the relations determining the partial freezing temperatures of each component, depending in general on all the mole fractions of the components. In general the relations mentioned above are different for each of the components, depending upon the chemical character of the other components composing the system. Because we are unable to describe these relations in general terms, we are forced to determine experimentally the parameters defining the equilibrium state of the system.

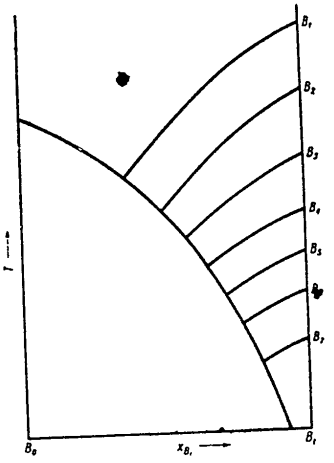

Fig. 1. Świętosławski's scheme for a series of eutectics formed by component B_0 and a series of compounds closely related chemically.

The problem becomes more simple when a series of eutectic systems is formed by chemically related compounds characterized by similar physicochemical properties. In connexion with this we suggest the division of all organic compounds forming simple eutectics into groups formed

by similar, chemically related compounds. Below we will consider exclusively systems composed of such compounds.

According to Święłosławski's [1] assumption, the partial freezing temperature of a given component depends exclusively upon its mole fraction in the solution and is not influenced by any other relations associated with the coexistence of other components of the system. In Fig. 1 these simplified relations are shown on a diagram.

Hence we may assume the existence of a certain function expressing the relation between the partial freezing temperature of the given component and its concentration. This function will, of course, determine the ideal curve of solubility.

2. Eutectic systems formed by chemically related compounds

Penkala has recently collected [2] experimental data showing that, in the first approximation, Święłosławski's assumption seems to be correct. On the basis of these facts further conclusions may be drawn for systems in which the components belong to the same group of structurally and chemically related substances. First of all, two compounds belonging to the same series and both having the same freezing temperature are characterized by the same ideal solubility curve (Fig. 2 substance B_1 and B_2). Next, when two components B_1 and B_2, for example, forming a two-component eutectic mixture $E_{B_1B_2}$ have the same freezing temperature $T_{B_1}=T_{B_2}$, the solubility curves of the eutectic mixture $E_{B_1B_2}$ and of the pure component B_3 are identical, if the freezing temperatures of B_3 and $E_{B_1B_2}$ are equal ($T_{B_3}=T_{E_{B_1B_2}}$). This relation is graphically represented in Fig. 2.

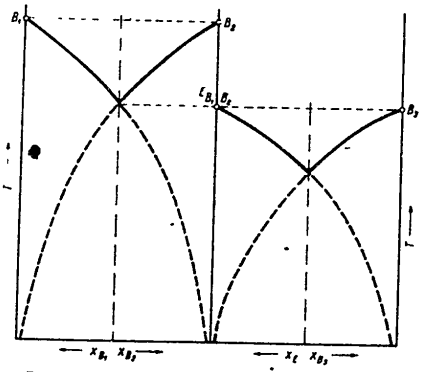

Fig. 2. Branches of a eutectic system formed by a pure component B_3 and a binary eutectic mixture $E_{B_1B_2}$, where $T_{B_3}=T_{E_{BB_m}}$ and $T_{B_1}=T_{B_2}$.

The conclusions given above may be treated as a basis for constructing a model of a hypothetical multicomponent eutectic system, in which all the components will have equal freezing temperatures. Assuming, just as for the two-component eutectic mixture $E_{B_1B_2}$, the identity of ideal solubility curves of pure components and those of multicomponent eutectic mixtures, if only the freezing temperatures of the pure component

and of the eutectic mixture are equal, one can show the correspondence between the constructed model of a hypothetical system and that of a real system whose components are characterized by different freezing temperatures.

3. Further consequences

The considerations mentioned above, as well as the analysis of the model, lead to the conclusion that for a given series of chemically related compounds a universal function may be found embracing all the solubility curves

$$T_i' = f\left(\frac{x_i}{m_i}\right). \tag{1}$$

In this equation T_i' stands for the partial freezing point of component i, x_i - denotes the concentration of that component, m_i - is a constant for the given component i and will be called a eutectic parameter of component i. Thus m_i does not depend upon the temperature. The validity of equation (1) depends on the degree of approximation introduced by the above assumptions. The use of this function should make it possible to determine the relation between the partial freezing temperatures and the composition of all the compounds involved. Function f should be considered as an unknown universal function characterizing the whole series of compounds under consideration. It is a function of one variable and may be represented by the ideal solubility curve. The stable part of the solubility curve in a given system fixed by the freezing temperatures of the pure component and of the eutectic mixture, may also be called a eutectic branch of component i. In the case of a three-component system the universal function (1) may be graphically represented by a cylindrical surface on a tridimensional diagram T, x_2, x_3, for k-component eutectic systems it will be represented by a hypersurface on a k-dimensional diagram.

Parameter m_i is defined by the limit conditions of relation (1). For $T_i' = T_i$, where T_i corresponds to the freezing temperature of the pure component i, $x_i = 1$. Consequently

$$T_i = f\left(\frac{1}{m_i}\right); \quad m_i = \frac{1}{f^{-1}(T_i)}; \tag{2}$$

where f^{-1} is reversed with respect to f, so that if $y = f(x)$, then $x = f^{-1}(y)$.

4. Conclusions

On condition that the freezing temperatures of the pure components are known, and that either the universal function or one of the solubility curves or even one branch of the eutectic system for a given component is known, it is possible to determine in a given range of temperature, the ideal solubility curves for all the components. In this way, too, it is

possible to give a full description of the equilibrium parameters for all of the two-three-and multicomponent eutectic systems formed by a series of chemically and structurally related substances.

We apply the term *ideal eutectic systems* to those simple eutectic systems which are composed of the above series of compounds, for which the equilibrium parameters are determined by the universal relation (1) expressing all the solubility curves. So equation (1) and the universal character of function f are the criteria of the ideality of a multicomponent eutectic system.

Summary

1. It is suggested to divide all organic compounds forming simple eutectic systems into groups of chemically related compounds.

2. A type of simple multicomponent eutectic system, formed by compounds closely related chemically, and called an ideal eutectic system, was described.

3. It was shown that in an ideal eutectic system a universal relation (1), determining the ideal solubility curves of individual components, is fulfilled.

DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF WARSAW

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CHEMISTRY

General Properties of Ideal Eutectic Systems. II

by

W. MALESIŃSKI

Presented by W. ŚWIĘTOSŁAWSKI on March 9, 1955

In a preceding paper [1] a classification of simple eutectic systems was given with the assumption that for a series of substances closely related structurally and chemically the relations determining the solubility curve may be expressed by the equation:

$$T_i' = f\left(\frac{x_i}{m_i}\right), \tag{1}$$

T_i' stands for the partial freezing temperature of component i being in equilibrium with the liquid phase containing x_i mole fraction of that component; m_i is a constant eutectic parameter of component i, its value does not depend upon the temperature. For two other deliberately chosen components at the equilibrium temperature we may write:

$$f\left(\frac{x_1}{m_1}\right) = f\left(\frac{x_2}{m_2}\right). \tag{2}$$

Because there is only one value x for a given component at a given equilibrium temperature, we conclude that

$$\frac{x_1}{m_1} = \frac{x_2}{m_2} \quad \text{or} \quad \frac{x_1}{x_2} = \frac{m_1}{m_2}. \tag{3}$$

Equation (3) expresses the relation existing between the two ideal solubility curves (called often eutectic branches), which may be formulated as follows: the ratio of the concetrations in the liquid phase of two deliberately chosen components in a two- three- or multicomponent eutetic system, being in equilibrium with pure solid phases of these components, remains constant. In other words, the ratio of the solubilities expressed in mole fractions of two components does not depend upon temperature. In Fig. 1 this relation is represented graphically. Consequently, if the values $m_i/m_j = k_{ij}$ are given, it is possible to draw

all of the curves representing the eutectic branches on the basis of the shape of one of them.

There is another consequence resulting from equation (1), namely, at any temperature, including the eutectic one, relation (3) remains unchanged for any pair of the components of the system. If we take into consideration a binary ideal eutectic system, viz., that at the eutectic point $x_1+x_2=1$, we may rewrite equation (3) in the following manner:

$$x_1=\frac{m_1}{m_1+m_2} \qquad x_2=\frac{m_2}{m_1+m_2}. \tag{4}$$

These two relations define the composition of the eutectic mixture, expressing it in terms of m_1 and m_2. For a k-component system the mole fraction of component i may be calculated in the same way

$$x_i=\frac{m_i}{\sum_{i=1}^{k} m_i}, \tag{5}$$

where m_i is the constant eutectic parameter of component i.

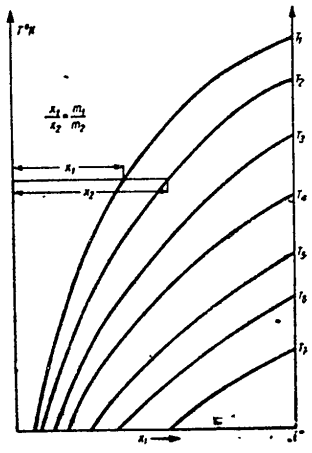

Fig. 1. Ideal solubility curves corresponding to the constant relation:

$$\frac{x_i}{x_j}=\frac{m_i}{m_j}=k_{ij}$$

Another property of the ideal eutectic systems consists in the general form in which the ideal solubility curve of the eutectic mixture may be expressed. Knowing that for a binary eutectic mixture in a system composed of any number of components $x_1/x_2=\text{const.}$, we may write:

$$x_1+x_2=x_{E_{12}}. \tag{6}$$

We call $x_{E_{12}}$ a mole fraction of the eutectic mixture of components 1 and 2. According to one of the conclusions given in a preceding paper [1], we may use for components 1 and 2 the following two relations:

$$x_1=m_1 f^{-1}(T'_1) \qquad x_2=m_2 f^{-1}(T'_2). \tag{7}$$

The intersection curve of two surfaces (7) expresses the solubility of the eutectic mixture E_{12}. Then at a given partial freezing temperature of eutectic mixture $T'_{E_{12}}$, both general equations (7) must be fulfilled:

$$x_1=m_1 f^{-1}(T'_{E_{12}}) \qquad x_2=m_2 f^{-1}(T'_{E_{12}}). \tag{8}$$

Combining equations (8) with (9) we obtain:

(9) $$x_{E_{12}} = x_1 + x_2 = (m_1 + m_2) f^{-1}(T'_{E_{12}})$$

or

(10) $$T'_{E_{12}} = f\left(\frac{x_{E_{12}}}{m_1 + m_2}\right).$$

A similar consideration leads us to the conclusion that the partial eutectic freezing temperature for an ideal eutectic mixture composed of k-components is expressed by the equation:

(11) $$T'_{E_k} = f\left(\frac{x_{E_k}}{\sum_{i=1}^{k} m_i}\right).$$

Let us consider the ideal solubility of the binary noneutectic mixture M_{12}, containing an excess of component 1 as compared with the composition of the eutectic mixture E_{12}. In this case the ratio of the mole fraction $\frac{x_2}{x_1} = a$ is constant and lower than that which corresponds to the eutectic mixture E_{12}. For this reason

$$a < \frac{m_2}{m_1}.$$

In the considered case:

(12) $$x_{M_{12}} = x_1 + x_2,$$

where $x_{M_{12}}$ denotes the mole fraction of mixture M_{12} in the solution.

Finally, we have:

(13) $$x_1 = \frac{x_{M_{12}}}{1+a}.$$

If equilibrium is established between the infinitesimal amount of component 1 and the solution (component 2 is found exclusively in the solution) the partial freezing temperature T_1 is represented by the equation:

(14) $$T'_1 = f\left(\frac{x_1}{m_1}\right).$$

Substituting (13), we obtain:

(15) $$T'_1 = f\left(\frac{x_{M_{12}}}{m_1(1+a)}\right).$$

Equation (15) represents the temperature at which the solid phase of component 1 disappears when the mixture M_{12} having a non-eutectic composition is dissolved in the solvent composed of all the components of the system except 1. If $a=0$, then $x_2=0$, $x_{M_{12}}=x_1$ and (15) is reduced to equation (14).

Summary

Starting with the general equation (1), some of the properties of eutectic systems composed of chemically and structurally related compounds were formulated. In particular, the following relations were given:

a) The solubility ratio of different compounds at the same temperature is constant and equal to the ratio $m_i : m_j$ of the eutectic parameters.

b) The composition of a k-component eutectic mixture is determined by the eutectic parameter in the following way:

$$x_i = \frac{m_i}{\sum_{i=1}^{k} m_i}$$

c) The solubility curves of the pure component and the solubility curve of the mixture of these components, having eutectic or non-eutectic composition, are expressed by the same universal function and by the same eutectic parameters characterizing individually each of the components. The parameters do not depend upon the temperature.

INSTITUTE OF PHYSICAL CHEMISTRY, POLISH ACADEMY OF SCIENCES.

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CHEMISTRY

Ternary Ideal Eutectic Systems. III

by

W. MALESIŃSKI

Presented by W. ŚWIĘTOSŁAWSKI on March 9, 1955

Several years ago Świętosławski [1], basing himself on experimentally established facts, suggested that ternary eutectic systems should be divided into two groups: ideal and non-ideal. In Fig. 1 a graphical presentation of an ideal ternary eutectic system is given. It can be concluded from the graph that the main property of an ideal ternary eutectic system consists in the following phenomena: three lines, AE_{BC}, BE_{AC} and CE_{AB}, which join points A, B and C of the concentration triangle with three others representing the composition of the three binary eutectics E_{AC}, E_{BC} and E_{AB}, cross one another at a common point E_{ABC}.

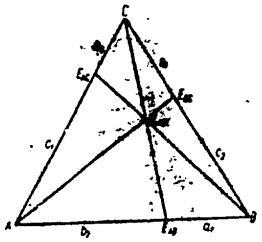

Fig. 1. Ternary ideal eutectic system

This condition is fulfilled when

$$a_1 b_1 c_1 = a_2 b_2 c_2. \tag{1}$$

In Fig. 1 the values a_1, b_1, c_1, a_2, b_2 and c_2 are graphically represented. They correspond to the mole fraction of each of the components in binary eutecticts. The condition that the ternary eutectic mixture is located in the common crossing point of the three lines is made clear by the following equations:

$$\frac{a}{b}=\frac{a_1}{b_2}; \qquad \frac{b}{c}=\frac{b_1}{c_2}; \qquad \frac{c}{a}=\frac{c_1}{a_2}. \tag{2}$$

Symbols a, b, c represent the mole fraction of the components in the ternary eutectic mixture. The question arises, however, as to whether the condition with regard to the general properties examined in the two previous papers [2] are fulfilled, if the ternary eutectic system

TABLE I

	Component	System	Parameter m	Composition of binary eutectic mixtures E_{AB} x°/₀ calc.	E_{AB} x°/₀ exp.	E_{BC} x°/₀ calc.	E_{BC} x°/₀ exp.	E_{BC} x°/₀ calc.	E_{BC} x°/₀ exp.	Composition of ternary eutectic mixtures x°/₀ calc.	x°/₀ exp.
1	A	1, 2, 3-trichlorobenzene	1.000	30.9	31	54.9	55.2	—	—	24.6	23
	B	1, 2, 4- „	2.24	69.1	69	—	—	73.1	72.5	55.1	56.5
	C	1, 3, 5- „	0.823	—	—	45.1	44.8	26.9	27.5	20.3	20.5
2	A	o-nitrophenol	1.000	72.2	72.5	75.7	75.5	—	—	58.7	57.7
	B	m- „	0.384	27.8	27.5	—	—	54.5	54.8	22.5	23.2
	C	p- „	0.321	—	—	24.3	24.5	45.5	45.2	18.8	19.1
3	A	o-nitroaniline	1.000	73.6	74.6	82.0	81.4	—	—	63.4	67
	B	m- „	0.358	26.4	25.5	—	—	62.0	63	22.7	20
	C	p- „	0.219	—	—	18.0	18.6	38.0	37	13.9	13
4	A	catechol	1.000	50.4	47	73.5	77	—	—	42.7	38
	B	resorcinol	0.984	49.6	53	—	—	73.2	70	42.0	43
	C	hydroquinol	0.360	—	—	26.5	23	26.8	30	15.3	19
5	A	o-chlorobenzoic ac.	1.000	58.1	57	86.4	86	—	—	52.9	52
	B	m- „ „	0.720	41.9	43	—	—	80.9	80	38.1	39
	C	p- „ „	0.173	—	—	14.6	14	19.1	20	9.0	9
6	A	o-chlorobenzoic ac.	1.000	56.2	57	64.2	65.5	—	—	28.2	25
	B	m- „ „	0.779	43.8	43	—	—	30.6	31.3	22.0	20
	C	benzoic ac.	1.780	—	—	63.8	64.5	69.4	68.7	49.8	55
7	A	2, 4, 6-trinitrotoluene	1.000	42.0	43	29.6	31	—	—	22.1	20.2
	B	2, 4-dinitrotoluene	1.38	58.0	57	—	—	39.1	40	30.5	31.8
	C	p-nitrotoluene	2.15	—	—	70.4	69	60.9	60	47.4	48.0
8	A	2, 4, 6-trinitrotoluene	1.000	12.4	12.4	31.0	31.0	—	—	9.7	9.5
	B	o-nit otoluene	7.06	87.6	87.6	—	—	76.0	76	68.6	69.5
	C	p- „	2.227	—	—	69.0	69.0	24.0	24	21.7	21
9	A	2, 4-dinitrotoluene	1.000	16.3	15.8	39.1	40	—	—	13.0	12.7
	B	o-nitrotoluene	5.14	83.7	84.2	—	—	76.7	76	66.8	68.7
	C	p- „	1.560	—	—	60.9	60	23.3	24	20.2	18.6

	A	o-nitrotoluene	1.000	54.7	52	80.7	76	—	—	45.7	42
10	B	m- ,,	0.339	45.3	48	—	—	69.6	67	37.8	44
	C	p- ,,	0.302	—	—	18.3	24	30.4	33	16.3	14
	A	sulphonal	1.000	60.2	39	9.5	10	—	—	3.3	6
11	B	naphtol	1.20	39.8	61	—	—	13.6	13	12.5	14
	C	salol	2.00	—	—	90.5	90	86.4	87	79.2	80
	A	di (o-nitrophenyl) carbonate	1.000	64.3	64.7	65.9	65.8	—	—	48.3	49.5
12	B	di (o-, p'-nitrophenyl) carbonate	0.555	35.7	35.3	—	—	51.8	52.5	26.8	23.8
	C	di (p-nitrophenyl) carbonate	0.517	—	—	34.1	34.2	48.2	47.5	24.9	26.7
	A	naphthalene	1.000	11.6	13.4	4.2	3.7	—	—	3.2	2.3
13	B	benzene	7.62	88.4	86.6	—	—	21.1	27.6	24.1	27.3
	C	m-xylene	38.000	—	—	95.8	96.3	78.8	72.4	72.5	70.4
	A	naphthalene	1.000	14.7	13.4	1.9	2.18	—	—	1.7	1.42
14	B	benzene	5.80	85.3	86.6	—	—	10.1	9.07	9.9	12.75
	C	toluene	51.6	—	—	98.1	97.82	89.9	90.93	88.4	85.76
	A	naphthalene	1.000	4.6	3.7	1.4	2.18	—	—	1.1	2.0
15	B	m-xylene	20.6	95.4	96.3	—	—	22.9	18	22.7	19.0
	C	toluene	89.9	—	—	98.6	97.82	77.1	82.0	76.2	79.0
	A	p-xylene	1.000	24.1	24.3	13.3	13.3	—	—	9.4	9.5
16	B	o- ,,	3.15	75.9	75.7	—	—	32.6	32.8	29.5	28.1
	C	m-xylene	6.52	—	—	86.7	86.7	67.4	67.2	61.1	62.4
	A	p-xylene	1.000	24.3	24.3	2.5	2.5	—	—	2.4	2.3
17	B	o- ,,	3.15	75.7	75.7	—	—	7.6	7.7	7.4	7.5
	C	ethylbenzene	38.43	—	—	97.5	97.5	92.4	92.3	90.2	90.2
	A	p-xylene	1.000	12.6	13.3	2.6	2.5	—	—	2.2	2.2
18	B	m- ,,	6.92	87.4	86.7	—	—	15.8	16.5	15.4	17.8
	C	ethylbenzene	37.0	—	—	97.4	97.5	84.2	83.5	82.4	80.0
	A	benzene	1.000	28.7	27	8.6	9.07	—	—	7.1	14.2
19	B	m-xylene	2.48	71.3	73	—	—	18.9	18.0	17.6	16.5
	C	toluene	10.65	—	—	91.4	90.93	81.1	82.0	75.3	69.3
	A	o-xylene	1.000	31.7	32.8	8.0	7.7	—	—	6.8	7.0
20	B	m- ,,	2.16	68.3	67.2	—	—	15.8	16.5	14.8	15.5
	C	ethylbenzene	11.45	—	—	92.0	92.3	84.2	83.5	78.4	77.5

is an ideal one according to Świętosławski's definition. For proving this, let us use the symbols m_1, m_2, m_3 for designating the constant eutectic parameters of the three components A, B, C. According to previous considerations [2], we may write the following equations:

$$(3)\qquad \begin{aligned} a_1&=\frac{m_1}{m_1+m_2}; & a_2&=\frac{m_1}{m_1+m_3};\\ b_1&=\frac{m_2}{m_2+m_3}; & b_2&=\frac{m_2}{m_1+m_2};\\ c_1&=\frac{m_3}{m_1+m_3}; & c_2&=\frac{m_3}{m_2+m_3}; \end{aligned}$$

which fulfill the condition that $a_1b_1c_1=a_2b_2c_2$.

On the other hand, we may express the composition of the ternary eutectic mixture in terms of values m_1, m_2, m_3 as follows:

$$(4)\qquad a=\frac{m_1}{m_1+m_2+m_3}; \qquad b=\frac{m_2}{m_1+m_2+m_3}; \qquad c=\frac{m_3}{m_1+m_2+m_3};$$

because:

$$(5)\qquad x_i=\frac{m_i}{\sum_{i=1}^{k} m_i}.$$

Then the number of components k is equal to 3.

It is easy to see that the conditions of equations (2) are fulfilled if the relations (3) and (4) are correct. In the same way it is possible to prove that Świętosławski's other scheme [3] given for quaternary and polycomponent systems is also correct. For instance, for an ideal eutectic system composed of five components A, B, C, D, F it is possible to consider that it is composed of component A and two binary eutectics E_{BC} and E_{DF}, or even of two components A and B and one ternary eutectic. In both cases Gibbs's concentration triangle may be used for graphical presentation of the phenomena taking place in those systems.

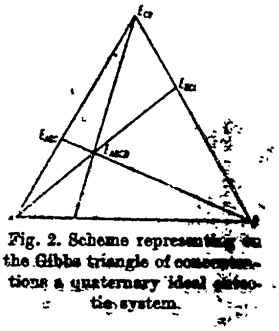

Fig. 2. Scheme representing on the Gibbs triangle of concentrations a quaternary ideal eutectic system

Because a relatively large number of ternary eutectic mixtures formed by chemically and structurally closely related substances have been examined [4] it is possible to determine whether or not these systems belong to ideal or almost ideal ones. The results are shown in Table I. The parameters m_i of the components have been calculated from the experimental composi-

tions of binary eutectic mixtures. In Table I the following data are given: a) the mean values of the parameters m, taking one of the components as reference compound ($m=1$), b) the compositions of the binary and ternary eutectics calculated from equations (3) and (4) in comparison with experimental ones.

It should be noted that in the case of five out of 20 systems (3, 4, 6, 10, 19) no satisfactory agreement was found. The differences between the calculated and the observed composition of ternary eutectics are less than 1% mole fraction for six systems (2, 5, 8, 14, 17, 20) and between one and three per cent for the nine remaining systems. The conclusion may be made that in this way the composition of ternary eutectic mixtures may be calculated with a satisfactory agreement. This is an indication that a large number of ternary eutectics formed by chemically or structurally related organic substances often form ideal or almost ideal systems.

Summary

1. The conditions expressed by equations (1) and (2) were given for defining the ideal eutectic systems described by Świętosławski.

2. It was shown that the general properties of ideal three- and polycomponent eutectics, examined in the two preceding papers [2] are in close agreement with those defined by Świętosławski.

3. A table is given showing that the composition of ternary eutectics formed by substances closely related both chemically and structurally may be calculated with a satisfactory agreement.

INSTITUTE OF PHYSICAL CHEMISTRY, POLISH ACADEMY OF SCIENCES.

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CHEMISTRY

The Change of the Mutual Exchange Ability of the Same Pair of Anions or Cations in Dependence on the Size of the Accompanying Ions. I

by

T. PENKALA

Presented by W. ŚWIĘTOSŁAWSKI on March 22, 1955

In a paper published in Roczniki Chemii, W. Świętosławski [1], [2] has given a scheme of gradual transition of organic compounds in binary mixtures from solid solutions with unlimited mutual solubility to ideal eutectics. This transition is correlated with the gradual increase of the difference in shape and size of the molecules of the substances in the binary systems. On the basis of an adequate comparison of experimental data collected from literature, it has been observed that the given scheme is also true for binary systems of inorganic compounds if we examine the increasingly difficult mutual exchange ability of the same pair of anions or cations in relation to the influence of the size of the accompanying ions. With the decrease of mutual exchange ability of the same pair of ions in the cristalline network we pass, conforming to W. Świętosławski's scheme, from solid solutions with unlimited mutual solubility to solid solutions with limited solubility, and finally to ideal eutectics with pure solid phases of the two components.

As Goldschmidt [3] and other authors [4] have shown for binary systems, mutual exchange ability appears in ions, the radii of which do not differ from each other by more than 15%. Goldschmidt has observed that the mutual exchange ability of the same pair of ions depends on the type of the space network and has demonstrated that in complicated structures of multiatom compounds there could appear significant structural gaps, which caused an increase of the mutual ion exchange ability. In binary systems of inorganic compounds characterized by a simple chemical composition and a simple structural type the influence of the size of cations on mutual exchange ability of the same pair of anions can be observed, as shown by the following examples.

Comparing three binary systems KOH-KF, NaOH-NaF and LiOH-LiF (Fig. 1), we can state that the mutual exchange of the same pair of anions occurs the easier, the greater are the cations bound with the anions. The radii of the ions in these systems and in the systems mentioned below are the following: $F' - 1.33$ Å, $OH' - 1.53$ Å, $Cl' - 1.80$ Å, $Br' - 1.96$ Å, $I' - 2.20$ Å, $Li^{\cdot} - 0.78$ Å, $Na^{\cdot} - 0.98$ Å, $K^{\cdot} - 1.33$ Å, $Ba^{\cdot\cdot} - 1.43$ Å, $Sr^{\cdot\cdot} - 1.27$ Å.

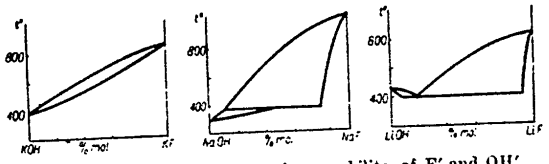

Fig. 1. Increase of mutual exchange ability of F′ and OH′ with the increase in size of cations

We also see the same relationship in the systems: 1) KOH-KCl, which forms a solid solution with a small miscibility gap; 2) NaOH-NaCl, which forms a solid solution with a significant greater miscibility gap; 3) LiOH-LiCl, which forms a eutectic (LiOH+3LiCl·2LiOH). This regularity occurs also in the systems: KCl-KI, which forms a solid solution, and NaCl-NaI, which forms a eutectic composed from the pure component NaCl and the solid solution Na(Cl, I).

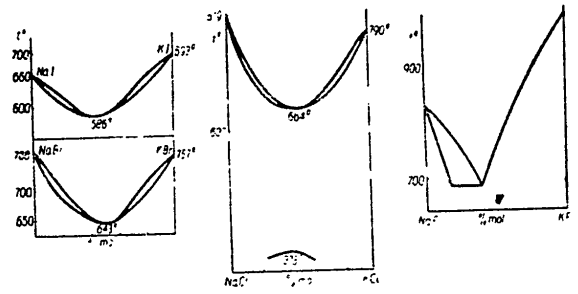

Fig. 2. The gradual decrease of the minimum point of the solidus curve is related with the miscibility decrease of the components in the solid solutions

Equally, the mutual exchange of the cations is the better the greater the anions. This relation is seen on the following example: (Fig. 2)

NaI-KI and NaBr-KBr form solid solutions, NaCl-KCl form a solid solution which undergoes, in lower temperatures, a partial separation, NaF-KF form a eutectic composed of the pure phase KF and mix-crystals (Na, K)F.

The example given on Fig. 2 evidences the relationship between the decrease of the miscibility of the components in the solid solutions and increase in curvature of the solidus curves in such a way that the minimum of the freezing temperature gradually decreases. The difference between the freezing temperature of the lower freezing component and the minimum point in the following mixtures are: KI-NaI — 74°, KBr-NaBr — 114°, KCl-NaCl — 126°. The increase of the concavity of the solidus curve can be found too in the solid solutions NaBr-LiBr and NaCl-LiCl. In the NaBr-LiBr system the minimum point of the solidus curve lies only 27° below freezing point of the lower freezing component. But in the NaCl-LiCl system the smaller anion depresses the mutual exchange ability of the same pair of cations: this appears in the fact that the minimum point lies 62° C. below the freezing temperature of the lower freezing component, and, besides, in lower temperatures the solution shows the demixing of the components.

A similar relationship, viz., the lowering of the minimum of the solidus curve with the decrease of miscibility of the components, is seen, in the systems formed by analogous salts of two valency metals. For example, the solidus curve of the solid solution $(Ba, Sr)F_2$ has a deeper minimum than the curve $(Ba, Sr)Cl_2$. The freezing points of the pure components are: BaF_2 — 1280°, SrF_2 — 1260°, $BaCl_2$ — 955°, $SrCl_2$ — 870°. In the $(Ba, Sr)F_2$ system the minimum point — 1080° lies 180°C. below the freezing point of the lower freezing component. In the $(Ba, Sr)Cl_2$ system the temperature at the minimum point — 847° — is only 23° C. below the melting point of $SrCl_2$. The observed regularity concerns binary systems of inorganic compounds which do not show too strong ionic polarization.

Summary

1. It has been observed on crystals of halide salts, which do not show too strong ionic polarization, that the greater the haloide ions, the easier the mutual cation exchange, and the greater the cations the easier the mutual exchange of the same pair of anions.

2. It has been found that W. Świętosławski's scheme concerning a gradual transition from solid solutions to ideal eutectics, is also true for binary systems of inorganic compounds in the case when mutual exchange of the same pair of ions becomes more and more difficult.

3. With the decrease of miscibility of the components in solid solutions the tendency to a gradual decrease of the minimum point of the "solidus" curve has been observed.

DEPARTMENT OF PHYSICAL CHEMISTRY, WARSAW UNIVERSITY

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CHEMISTRY

The Gradual Transition from Solid Solutions to Eutectics in Binary Systems of Inorganic Compounds. II

by

T. PENKALA

Presented by W. ŚWIĘTOSŁAWSKI on March 22, 1955

In the preceding paper [1] it has been demonstrated that the scheme given by W. Świętosławski concerning the gradual transition from solid solutions without miscibility gap through solid solutions with miscibility gap to ideal eutectics (Fig. 1), is true in the case of gradual increase of the difference in structure and size of the molecules in the organic substances which form binary systems.

In this paper the literature data concerning binary systems of monovalent metal chlorides has been collected and a gradual transition from solid solutions to ideal eutectics, similar to W. Świętosławski's scheme for organic compounds, has been observed.

In organic compound systems the formation of a solid solution or a eutectic depends, according to the investigations of Goldschmidt [4], [5], on the crystal-chemical resemblance of the ions; this resemblance is correlated with the ionic radius size and the polarization tendency of the ions. In halide salts of monovalent metals the weakest polarization is shown by fluorides and chlorides, since the polarization of the anions increases with their dimensions. In these systems the decisive factor which influenced the formation of solid solutions is the size of mutual exchanging ions, in the same way as the size of molecules in molecular networks of organic compounds. Hence the relationship given by W. Świętosławski for organic compound systems is also true in case of binary systems of ionic compounds with a not too strong ionic polarization. In the examined series of binary

Fig. 1. W. Świętosławski's scheme of gradual transition from solid solutions to eutectics in organic compound systems

systems, shown on Fig. 2, a gradual transition from solid solutions without a miscibility gap to eutectics through solid solutions with a minimum, can be observed. These solutions show in the lower tem

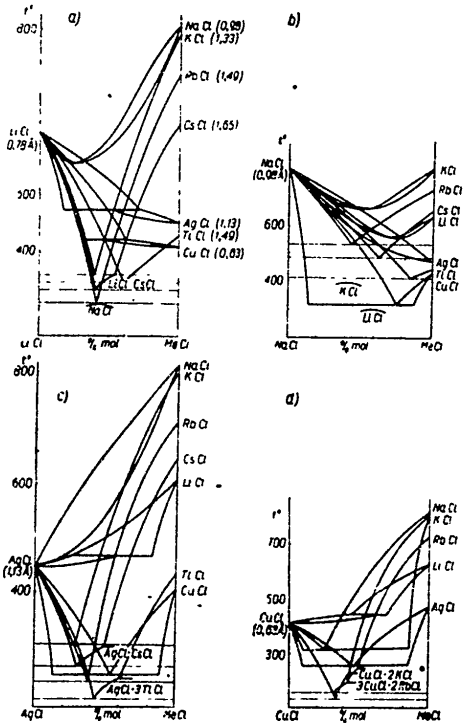

Fig. 2. Mutual exchange ability of monovalent cations in crystalline networks of metal chlorides. In parenthesis the cation radii, in Å

perature range a spontaneous demixing of the components (Fig. 2*b*) or a gradual extension of the miscibility gap when the difference in size of the cations increases (Fig. 2, *c*, *d*).

The relationship discussed, regarding the gradual transition from eutectics to solid solutions is also true in case of mutual exchange of anions (Fig. 3).

In the systems discussed it can be observed that in case of a common anion and a great difference in size of the cations double salts are

formed and the eutectics are composed of double salts and of the main component (Fig. 2 *a*, *c*, *d*). In the case of a large difference in size of the anions in binary systems of salts with a common cation a similar influence has been noticed. For example, the NaOH-NaCl system forms a solid solution, NaOH-NaBr, an ideal eutectic of the components, but in the NaOH-NaI system a eutectic NaOH+3NaI·2NaOH is formed.

It has been noticed that there is a reduction of miscibility of the components in the solid solutions when the tendency to depress the solidus curve minimum increases. With the increase of the difference in

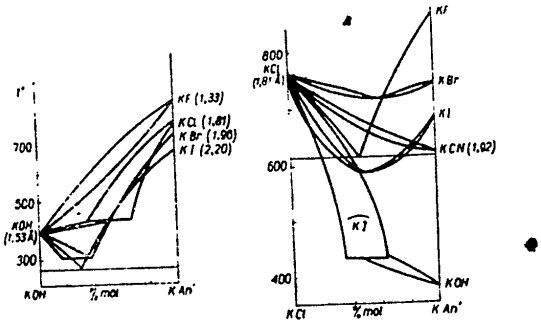

Fig. 3. Gradual transition from solid solutions to eutectics in the case of mutual exchange of anions. In parenthesis: the anion radii figures

size of the anions in the solid solutions K(Cl, CN), K(Cl, Br), K(Cl, I) shown in Fig. 3, the solidus curve minimum gradually decreases. Similarly the solid solution (Na, Ag)Cl shows no minimum, but with greater difference in cation size, the miscibility in the (Na, K)Cl and (Na, Li)Cl solutions is lower, which is seen in the demixing into components of solid solutions at lower temperatures and the disappearance of a minimum on the solidus curve (Fig. 2 *b*).

In the case of gradual transition from solid solutions without miscibility gap to eutectics, caused by increased difference in ion size, there can be distinguished the following intermediate stages:

1) solid solutions without a minimum;

2) solid solutions with a minimum, which in lower temperatures do not undergo demixing into components and have the tendency to an increasing depressure of the minimum point with the increase of the difference in dimensions of the exchanging ions;

3) solid solutions which separate into components at lower temperatures;

4) solid solutions with a minimum, which show a separation into components at temperatures near to that minimum;

5) solid solutions which demix into components at temperatures equal to the minimum temperatures;

6) solid solutions with a small miscibility gap, the formation of which is associated with a more distinctly pronounced miscibility gap so that its peak is found in the liquid phase area;

7) solid solutions with a large miscibility gap;

8) ideal eutectics of the components;

9) eutectics formed by a double salt and one of the components.

Summary

1. It has been observed that the scheme given by W. Świętosławski concerning the gradual transition of binary mixtures of organic compounds from solid solutions through solid solutions with limited mutual solubility to ideal eutectics may also be applied to inorganic ionic compounds without or with a weak ionic polarization.

2. A gradual increase in curvature of the solidus curve in case of the solid solutions with a minimum and a gradual transition through solid solutions with mutual solubility to eutectics of solid solutions has been pointed out.

3. In binary mixtures of metal chlorides with common anion and great difference in size of the cation, the formation of a eutectic double salt and of the main components is cleary pronounced. A similar influence in case of a large difference in size of the anions in binary mixtures of salts with common cation is evident.

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CHEMISTRY

The Influence of Ionic Polarization on the Formation of Solid Solutions and Eutectics. III

by

T. PENKALA

Presented by W. ŚWIĘTOSŁAWSKI on March 22, 1955

The negative influence of ionic polarization on the formation of solid solutions confirmed by Goldschmidt [1], [2] can be investigated on the basis of the scheme given by W. Świętosławski [3], [4] concerning the gradual transition from solid solutions to eutectics and organic mixtures. This scheme is also valid for binary systems of inorganic compounds with not too strong ionic polarization. Deviations from this scheme indicate the influence exerted by ionic polarization.

In Fig. 1 binary systems composed by AgI and iodides of other metals of the first group in the periodical system have been shown. According to Goldschmidt [2] the Ag ion caused a very strong polarization activity on the large iodine anion so that the distance between the centres Ag and I ions is smaller than the sum of the radii of these ions. Hence at the formation of solid solutions by AgI and other iodides, the Ag ion behaves as if its radius were smaller.

The Ag ion substitutes the much smaller Li and Cu ions in solid solutions of (Ag, Li)I and (Ag, Cu)I, but do not substitute the Na ion in the AgI-NaI system, although the Na ion is similar in size. A similar relationship can be observed in binary systems formed by NaI-KI and NaI-AgI. There exists a solid solution of (Na, K)I although the difference in size of the cations is considerable, but the NaI-AgI system forms a eutectic, although the difference in size of the cations here is rather smaller.

In binary systems of bromides of monovalent metals, we can find some deviations, which confirm the negative ionic polarization influence on the miscibility of components with similar ionic dimensions. And so there exists a solid solution of (K, Na)Br, but KBr and AgBr form a eutectic, although the difference in size of the cations is here smaller.

In case of binary systems without ionic polarization the mutual exchange of the same pair of cations takes place more easily if the halide

ions are larger. For example, there exist solid solutions of (K, Na)I and (K, Na)Br, while the solid solution of (K, Na)Cl, in lower temperatures undergo, demixing into pure components, and the KF-NaF mixture

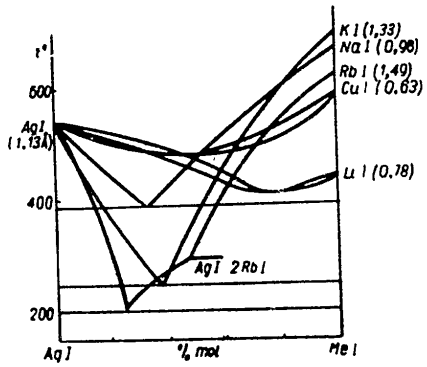

Fig. 1. Binary systems of AgI and iodides of monovalent metals. In parentheses, the radii of the cations in these systems, in Å

forms a eutectic KF+(Na, K)F. In binary systems of halide salts, in which one of the cations caused a strong polarization, this relationship does not take place. For example: the NaI-AgI system forms a eutectic, while the same pair of cations bound with smaller ions forms solid solutions of (Na, Ag)Br and (Na, Ag)Cl.

Summary

Deviations from the scheme of gradual transition from solid solutions to ideal eutectics in the case of binary systems of ionic crystals with strong ionic polarization has been observed. These deviations show a certain regularity, viz., the cation with a strong polarization behaves in binary systems as if its size were much smaller than indicated by the figures in the tables of experimentally determined size of ionic radius

DEPARTMENT OF PHYSICAL CHEMISTRY, WARSAW UNIVERSITY

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CHEMISTRY

On the Distillation Anomalies Observed in Mixtures of Components Forming Ternary Positive-Negative Azeotropes and Zeotropes. I

by

W. ŚWIĘTOSŁAWSKI and W. TRĄBCZYŃSKI

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of May 16, 1955

1 **Observations of Ewell and Welch.** In 1945 some interesting phenomena were described by Ewell and Welch [1] with regard to ternary systems in which two of the components formed with each other a binary negative azeotrope and with the third, a ternary zeotropic or azeotropic mixture. Owing to the shape of the tridimensional boiling temperature isobar ($p = 1$ atm.), a top-ridge curve divided the Gibbs triangle of concentrations into two parts. Only one system, that composed of chloroform, acetone and methanol, formed a positive-negative azeotrope. The latter still represents a unique example of a ternary saddle azeotrope which does not contain water. According to the classification suggested by one of us [2], it belongs to the first group, and its formation is due to the differences in the van der Waals forces acting between the molecules of the three components.

The anomaly taking place in the course of a fractional distillation of mixtures, forming systems characterised by the presence of a top-ridge condensation temperature isobar consists in the forming of several distillation levels, one of which, found in the middle or not far from the last level, is characterised by a lower condensation temperature than that of the two neighbouring ones.

Several years later Lang [3] confirmed the existence of these anomalies. In both the above-mentioned papers, however, no observations were made with regard to the changes in composition of the fractions collected and of the bottom products remaining after each successive removal of the distillate. Another paper of Haase and Lang did not contain either sufficient data [3]. Because of that, no graphical presentation could be made of the gradual changes in the composition of the fractions collected and of mixtures found in the flask and in the column.

2. Behaviour of Ternary Positive-Negative Azeotropes Belonging to the Second Group. The purpose of the present investigation was to examine the behaviour of a new group of ternary positive-negative azeotropes formed by a weak organic (acetic) acid, *A*, a weak organic (pyridine) base, *P*, and a hydrocarbon, *H*. In our case this last was the normal octane. Starting with 1952, a relatively large number of ternary saddle azeotropes of this kind were examined in our laboratory and some of them were described [4], [5], [6], [7]. They did not contain water and the negative azeotrope [(−)A, P] was formed as a result of the chemical acting forces of an acid and a base.

For the first example there was chosen a saddle azeotrope in which the top ridge condensation temperature isobar lay not far from the line *HC*, as shown in Fig. 1. In addition, the point (±)*Az*, corresponding to the composition of the ternary saddle azeotrope, is located closer to point *H* and somewhat higher than point M_P, which lies also on the top-ridge curve but corresponds to the maximum convexity of the top-ridge line. Its location is higher compared with other mixtures represented graphically by the same top-ridge curve HM_PC.

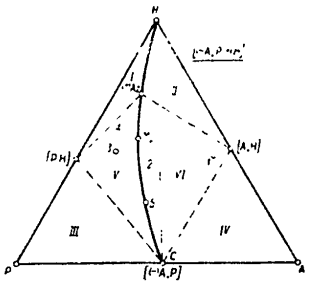

Fig. 1. Distillation fields of a ternary positive negative azeotrope [(−)*A*, *P*(+)*H*], all of them, except *V* and *VI*, form triangles. Fields *V* and *VI* are separated by the top-ridge curve $H(\pm)Az\,M_PC$. It is assumed that section $H(\pm)Az$ is practically a straight line.

There is another factor which exerts an influence on the distillation anomalies in the case of the saddle azeotropes examined in our laboratory. It consists in the large variety in shapes of the top-ridge condensation temperature isobars and in the locations of point (±)*Az*, corresponding to the composition of the ternary positive-negative azeotropes. In this investigation we chose the case graphically presented in Fig. 1.

3. Distillation Curves and Material Balance of Distillate Fractions and Mixtures Remaining in the Flask and in the Column. In Fig. 1, points 1, 2, 3, 4 and 5 represent the respective compositions of the initial mixtures submitted to fractional distillation. All details concerning these five distillations, including the analytical methods used for determining the compositions of the numerous fractions collected, will be published elsewhere. In this paper are described the most interesting experiments observed in the course of fractional distillation of the mixtures represented by points 4 and 5.

The distillation curves are shown in Figs. 2*a* and 2*b*. The concentration triangles are presented in Figs. 3*a* and 3*b*; in each of them curves *i*

and *II* correspond to the compositions of the fractions collected (*I*) and of the remaining material (*II*) found in the flask and in the distilling column.

It should be noted that point 4 lies between points $(\pm)Az$ and M_P. Point 5 is located on the top-ridge curve below M_P.

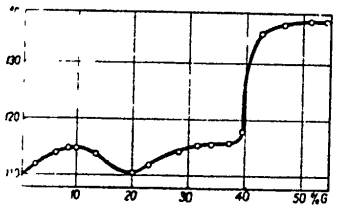

Fig. 2*a*

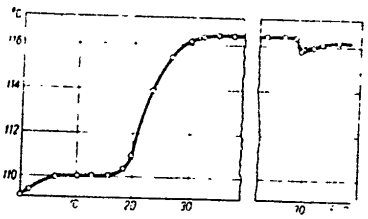

Fig. 2*b*

Figs. 2*a* and 2*b*. Distillation curves of mixtures 4 and 5. No horizontal level corresponding to the boiling temperature of the positive azeotrope $[P, H]$ is found on curve 2*b*. A pronounced temperature decrease corresponds to the moment when the total reflux has been established in the column.

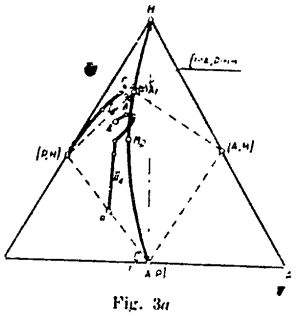

Fig. 3*a*

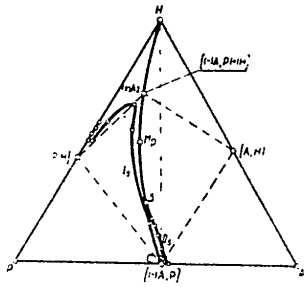

Fig. 3*b*

Figs. 3*a* and 3*b*. The compositions of the fractions collected when distilling mixtures 4 and 5, are shown on curves I_4 and I_5, and those of the bottom mixtures found in the flask and in the column (hold up) are represented by curves II_4 and II_5.

At the beginning of the fractional distillation of mixture 4 the positive binary azeotrope $[P, H]$ was collected in the receiver. Section *A* on the "bottom product curve" II_4 is practically a straight line. In the next stage the fractions collected (section *C* on curve I_4) have the composition equal or nearly equal to that of the ternary saddle azeotrope $(\pm)Az$. The flat surface of this part of the tridimensional isobar, as well as the analytical errors in determining small amounts of the fractions collected must be considered as responsible for the dissipation of the points lying in the flat regions. At this stage of the distillation the

position of the mixture found in the flask and in the hold-up of the column underwent changes, so that at the end of the distillation point B was reached. This point lies practically on the straight line connecting point $[P, H]$ with $[(-)A, P]$. At that moment there was not enough liquid to continue the distillation. One may assume, however, that a "straight line" distillation would have been followed, associated with a new drop in the condensation temperature. This would be associated with the distillation of azeotrope $[P, H]$ and afterwards with that of the negative one.

The fractional distillation of mixture 5 has been associated with the particularities shown in the graph of the two curves I_5 and II_5 (Fig. 3*b*). No horizontal levels were found in the course of the fractional distillation represented by the curve in Fig. 2*b*. Instead, a series of middle fractions appeared, which corresponded to mixture of $[P, H]$ and $(\pm)Az$ with an excess of the positive azeotrope in the first stage, and a decrease in the concentrations of $[P, H]$ in the second stage. Afterwards, the saddle azeotrope $(\pm)Az$ was collected and at the end of the distillation a mixture very similar to the composition of the negative azeotrope was found in the distillate.

The shape and the location of curve II_5 show the compositions shifting towards the left side of the main line HC. This corresponds to the higher concentrations of acetic acid compared with the last sections of curve I_5. It is probable that some thermal decomposition of the liquid in the flask was responsible for this shifting. It may be, however, that during that part of the distillation a new anomaly had appeared so that more pyridine passed into the receiver during the last stages of the distillation. Owing to this, both curves I_5 and II_5 have been shifted to the left side of the triangle.

It should be noted that a relatively large section of the distillation curve I_5 practically merged with the top-ridge condensation temperature isobar HM_PC.

We wish to express our thanks to W. Michalek for helping us with the distillation experiments and with the analytical work.

Summary

1. The recently investigated new group of ternary, positive-negative azeotropes, containing a weak organic acid, a weak organic base and a hydrocarbon, shows distillation anomalies similar to those found for a known saddle azeotrope composed of chloroform, acetone and methanol (*I*).

2. The saddle azeotropes (±)A_5 containing acetic acid, *A*, pyridine, *P*, and normal octane, *H*, contains less pyridine than the mixture represented by point M_P, which lies on the top ridge isobar and corresponds to the mixture characterised by its maximum convexity. The top ridge curve is located closer to the main line HC as compared

3. The material balance of the fractions collected (curves I_4, I_5) and of the mixtures remaining in the flask and in the column (curves II_4, II_5) was presented graphically in Figs. 3*a* and 3*b* for the two most interesting cases (points 4 and 5 in Fig. 1).

4. In the case of the fractional distillation of the mixture represented by point 4, it was found that at the end of the distillation the bottom product in the flask corresponded to a mixture of the negative azeotrope [(—)*A*, *P*] and the positive one. [*P*, *H*]. The last section of curve II_4 is a straight line inclining under an acute angle to the main line *HC*.

5. The fractional distillation of mixture 5 (Fig. 1), represented by point 5 lying lower than *MP* showed abnormal distillation phenomena in the first stage of the distillation. At the end, both the last fractions collected (I_5) and the mixtures found in the flask after each partial distillation (II_5) were shifted towards higher concentrations of acetic acid (*A*) as compared with the content of *A* in the negative azeotrope formed by *A* and *P*. It may be that this phenomenon was associated with some thermal decomposition of the residue in the flask.

PHYSICOCHEMICAL INSTITUTE OF THE POLISH ACADEMY OF SCIENCES
DEPARTMENT OF PHYSICAL CHEMISTRY OF ORGANIC RAW MATERIALS

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CHEMISTRY

A Method for Determining the Composition of Quaternary Azeotropes and the Position of Heteroazeotropic Lines

by

K. ZIĘBORAK and A. GALSKA

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of May 13, 1955

1. Introductory remarks.

A method for determining the composition of quaternary azeotropes was suggested recently by Świętos'awski [1]. This paper resulted from Zięborak's [2] observation that some paraffins such as isooctane, *n*-heptane, and cyclohexane, form quaternary azeotropes with benzene, ethanol and water. In this paper another method for examining the composition of quaternary heteroazeotropes is presented. This method may be applied in all cases in which the determination of the concentration ratio of two components, e. g., $B:C$, for an azeotrope obtained by fractional distillation is an easy operation. First, it is necessary to find the position of the heteroazeotropic line on the models shown in Figs. 2 and 3. Once that is done, the composition of the azeotrope under examination may be found by determining the composition of only one of the components in the azeotrope obtained by careful fractional distillation.

2. Preparation of substance.

In our investigation the system composed of benzene (B) – cyclohexane (C) – ethanol (E) – water (W) was chosen. Both benzene and cylohexane were thoroughly purified by rectification of the chemically pure reagents. The benzene sample was found to be of the fifth degree of purity, according to the ebulliometric scale [3]. In fact the difference between the boiling and the condensation temperatures δt was equal to 0.002°C. Cyclohexane of the fourth degree of purity was obtained ($\sigma t = 0.009$°C).

3. Methods of investigation.

Two Święlosławski ebulliometers were used, one differential, the other one-stage for controlling pressure changes. Measurements were taken in a strictly comparative way as described in Święlosławki's monograph [3].

4. Ternary system (*C*, *E*, *W*).

First of all the position of the heteroazeotropic line in the ternary system (*C*, *E*, *W*) was determined. Mixtures of cyclohexane and ethanol, their composition being indicated in the concentration triangle by points *D'*, *D''* and *D'''* (Fig. 1) were successively introduced into a differential ebulliometer. Next, small portions of water were added, the boiling and condensation temperatures of the mixtures being observed after each addition. In three successive series of measurements A_1, A_2, A_3 (upper part of Fig. 1) curves were obtained which showed abrupt minima of temperatures t_b and of condensation temperatures t_c. These minima corresponded to the crossing point of the heteroazeotropic line. Thus, by projecting these minima on to Gibbs' concentration triangle (Fig. 1) the position of the heteroazeotropic line *FGI* of the ternary (*C*, *E*, *W*) system was graphically represented.

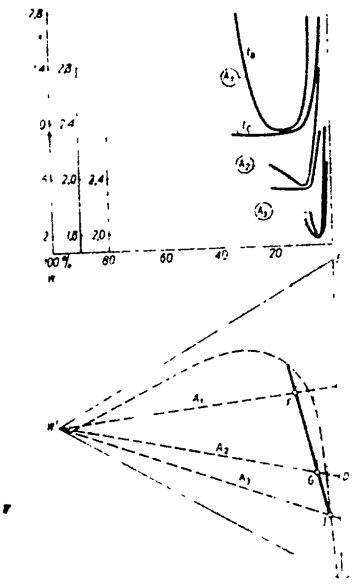

Fig. 1. Determination of the position of the heteroazeotropic line *FGI* in the system cyclohexane (*C*) ethanol (*E*)-water (*W*). The upper part shows the changes in the boiling temperature t_b and in the condensation temperature t_c caused by the change in the water content of the mixture.

The boiling temperature azeotrope of (*C*, *E*, *W*) was found to be equal to 62.60°C±0.05°C. The mixture represented graphically by point *I* was rectified, the cyclohexane content was determined in the distillate, and the contents of the other components were computed on the basis of the diagram (Fig. 1). The composition of the azeotrope under examination, expressed in weight per cent was as follows: 75.5% (*C*), 18.7% (*E*), 5.8% (*W*).

5. Quaternary system (*C,B,E,W*).

The geometrical representation of any property of a quaternary system may be realised in different ways, one of these ways being by the methods proposed by Fiodorov, Boecke, Radischchev [4]. When it is necessary to define the composition of a quaternary mixture, then a tetrahedron is mostly used. If, however, some properties of the system are to be represented, projections onto the tetrahedron are used. While examining the system under consideration, it was observed that among the four corresponding ternary systems:

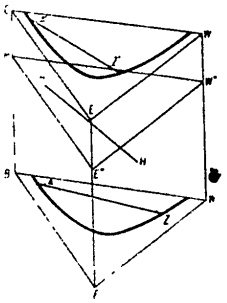

Fig. 2. A regular triangular prism; *B* - benzene, *E* ethanol, *W* water, *C* cyclohexane, *AZ* and *AZ'* the heteroazeotropic lines in the (*B, E, W*) and (*C, E, W*) azeotropes; *HH'* the heteroazeotropic line of the quaternary azeotrope (*B, C, E, W*).

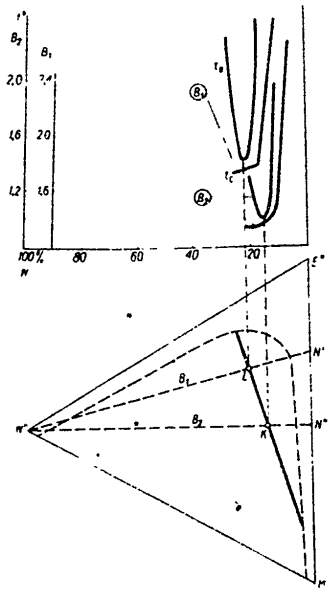

Fig. 3. Determination of the position of the heteroazeotropic line in the *ME' W''* section for which the ratio *BM*:*MC* const.= 2.7; t_B and t_C boiling and condensation temperature isobars measured by a Świętosławski ebulliometer.

(*B, E, W*); (*C, E, W*); (*B, C, E*); (*B, C, W*) two are very similar to each other, namely the (*B, E, W*) system investigated by Barbaudy [5] and the (*C, E, W*) one just described. In both these systems ethanol plays the rôle of a homogeniser because both benzene and cyclohexane are practically insoluble in water. Moreover, the azeotropes (*C, E, W*) and (*B, E, W*) are characterised by lower boiling temperatures than the two others. The specificity of the (*C,B,E,W*) system leads us to use a regular triangular prism for representing the composition of quaternary mixtures (5 - 9).

In a further continuation of the experimental work, the position of the heteroazeotropic line lying in the *MEW* section of the regular

prism was determined (Fig. 2). This section corresponds to quaternary mixtures characterised by a constant concentration ratio of cyclohexane and benzene. As mentioned above, this ratio may be determined quite easily (2). For the quaternary azeotrope it was as follows; $BM:CH=2.7:1$. The results of our measurements are represented on the concentration triangle (Fig. 3); the mixture of cyclohexane and benzene, being constant, may be considered as one component. The position of the "heteroazeotropic line" in a quaternary system is medial to its position in the corresponding (B, E, W) and (C, E, W) systems, as shown in (Fig. 4).

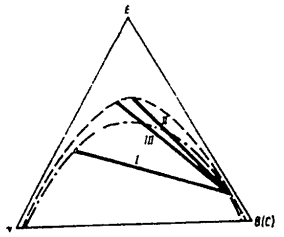

Fig. 4. Projections of the heteroazeotropic lines *I, II, III* on the prism plane (Fig. 2) corresponding to the (B,E,W), (C,E,W), (B,C,E,W) systems

In order to determine more precisely the inclination of the heteroazeotropic line *III* in a quaternary system in relation to the two others (*I* and *II*), two series of measurements were carried out, in which the boiling and the condensation temperatures were determined for four-component mixtures formed by mixing three-component mixtures, represented on the model (Fig. 2) by points. *A* and *Z* on one side and *A'* and *Z'* on the other. In both cases the minimum boiling temperatures were found, and these enabled us to determine more precisely the position of the heteroazeotropic line *HH'*.

Finally, the quaternary azeotrope was prepared by careful rectification on a column provided with a special head for the distillation of heteroazeotropes. The weight per cent composition of this azeotrope was determined and was as follows: 54.3%(*C*), 19.2%(*E*), 6.1%(*W*), 20.4%(*B*).

Summary

1. The composition of a quaternary heteroazeotrope formed by cyclohexane (*C*) benzene (*B*), ethanol (*E*), and water (*W*) was determined. Its composition expressed in weight per cent is as follows: 54.3% *C*, 20.4% *B*; 19.2% *E*, 6.1% *W*, and its boiling temperature is 62.14°C (± 0.05°C). These data differ slightly from those given earlier [2].

2. A method was described for the ebulliometric determination of the position of the heteroazeotropic line in a quaternary system. This method is based on determination of the concentration ratio of two of the components, those that are most closely related as regards their physicochemical properties. In the case under consideration these were benzene and cyclohexane.

3. A model of a regular triangular prism was used for representing a four-component system in which two substances are present, not mixing with the third one. Such a method of system representation facilitates the construction both of tie- and heteroazeotropic lines.

4. The composition of the ternary heteroazeotrope (*CEW*) was determined. It contains in weight per cent: 75.5% C; 19.7% *E*; 4.8% *W*; and is characterised by a boiling temperature of 62.60°C. The heteroazeotropic line forms the smallest acute angle with side *EC* (Fig. 4).

We express our thanks to Professor W. Świętosławski for his valuable advice.

DEPARTMENT OF BASIC ORGANIC RAW MATERIALS,
PHYSICOCHEMICAL INSTITUTE, POLISH ACADEMY OF SCIENCES

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CHEMISTRY

Azeotropic and Polyazeotropic Systems. XXI. A Series of Saddle Azeotropes Formed by Acetic Acid, Pyridine and Paraffinic Hydrocarbons

by
K. ZIĘBORAK

Presented by W. ŚWIĘTOSŁAWSKI on August 18, 1955

1. Introductory remarks

Some years ago Świętosławski [1], [2] classified negative binary and positive-negative azeotropes with no water as component. Since 1951, a number of ternary systems belonging to the latter group have been investigated in our department, but only a few numerical data have been published [3], [4], [5]. The present publication concerns a series of saddle azeotropes which are formed in ternary systems consisting of one non-polar component (a normal paraffinic hydrocarbon) and of two polar components, these being acetic acid and pyridine forming a binary negative azeotrope [( )(A, P)].

2. Experimental metods and substances used

In the present investigations, the method of ebulliometric measurements was used [2], [5]; a three stage differential Świętosławski's ebulliometer was applied [7]. Sufficiently pure and dehydrated acetic acid and pyridine were prepared. Normal paraffins were prepared from syntane fraction by removing unsaturated hydrocarbons and submission to two successive fractional distillations. Further details concerning the method will be published in Roczniki Chemii.

3. Results obtained

First to be investigated was the ternary system composed of *n* heptane, acetic acid and pyridine, in which the formation of a saddle azeotrope was proved. Table 1 gives numerical data concerning this system. They show some improvement on those published in a previous publi-

cation [3]. Fig. 1 represents the projection of the top-ridge line on the concentration triangle in this system, together with a probable location of the bottom concavity line joining two points corresponding to the composition of the two positive azeotropes $[P, H_1]$ and $[A, H_1]$ boiling at $t_{P,H}$ and $t_{A,H}$.

Next, in the same way, the system composed of *n*-octane, acetic acid and pyridine, as shown in Fig. 2, was examined by Brzostowski [8]. In this system, not only is the location of top-ridge line designed by the

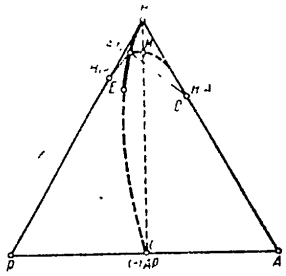

Fig. 1

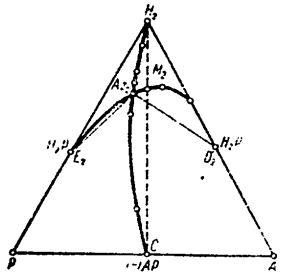

Fig. 2

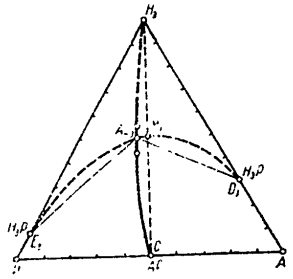

Fig. 3

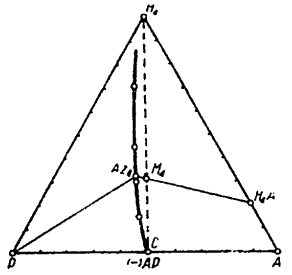

Fig. 4

Figs. 1 – 4. A series of ternary diagrams. On each of the concentration triangles, *A*, *P* and *H* represent acetic acid, pyridine and one of the paraffinic hydrocarbons of series (*H*). H_1 is *n*-heptane, H_2 *n*-octane, H_3 *n*-nonane, H_4 *n*-decane. At the same time, the three sides of the triangle represent the projections of the boiling temperature isobars examined by the use of the ebulliometric method. Points *E*, *D*, and *C* correspond to the concentration of two binary positive azeotropes and one negative. The line joining *H* with *C* is called the main line. This coincides with the projection of the boiling temperature isobars obtained for mixtures of $[(-)(A, P)]$ with *H*. For designating the minimum boiling temperature on this isobar, symbol *M* is used. $HAzC$ is the projection of the top ridge curve on the concentration triangle. Point Az represents the composition of the ternary positive-negative azeotrope.

method described by Świętosławski [2], but also the shape of the boiling concavity isobar $E_2Az_3M_2D_2$ was ebulliometrically examined. The composition of the saddle azeotrope in this and further systems was then ascertained by means of a fractional distillation of an appropriately chosen mixture. The composition of the fractions collected were verified by complete chemical analysis.

The system composed of *n*-nonane, acetic and pyridine, was investigated by Drozdowska [8]. In this system the binary azeotrope composed of *n*-nonane and pyridine is almost tangent. It is characterized by the azeotropic depression of 0.22°C. The projection of the top-ridge line CAz_2H_3 on the concentration triangle APH_3 is, as in the previous systems, slightly shifted from the main line CH_3 towards the left side of the triangle. The system composed of *n*-decane, acetic acid and pyridine was examined by Turski [8]. It is characterized by one binary positive azeotrope $[H_4A]$ and one positive zeotrope $[H_4P]$. In spite of the latter, a saddle azeotrope Az_4 was found, as shown in Fig. 4.

We were able to prove that *n*-undecane also forms a ternary positive-negative azeotrope with acetic acid and pyridine; we found, however, that the substances used in these experiments were not sufficiently pure. This system will be reexamined once more and the numerical data will undergo verification.

In Table I are listed the boiling temperatures and compositions of the ternary positive-negative azeotropes $[(-)(A,P)(+)H_i]$, examined, the latter being expressed both in weight and mole per cent.

TABLE I

Boiling temperatures and compositions of positive-negative azeotropes

Name of system	Boiling temp. of saddle azeotrope in °C.	Composition — weight per cent			Composition — mols per cent		
		A	P	H_i	A	P	H_i
Acetic acid — pyridine and *n*-heptane*)	96.5	34	10.6	86.0	5.0	12.8	82.2
n-octane	115.7	10.4	20.1	69.5	16.6	24.6	58.8
n-nonane	128.0	20.9	29.3	49.8	31.2	33.6	35.2
n decane	134.1	31.4	38.2	30.4	43.0	39.6	17.4

*) values verified and somewhat changed.

Table II shows the compositions and boiling temperatures of corresponding binary azeotropes. As regards the azeotropes formed by ace-

acid and a series of normál paraffins, Kurtyka's data [6] were used The boiling temperature isobars formed by pyridine with corresponding paraffins were examined by ourselves.

TABLE II

Binary positive azeotropes of pyridine and acid with normal paraffinic hydrocarbons

System of azeotropes (P, H_l) and (A, H_l)	Azeotrope boiling temperature — °C	Composition- weight per cent H_l	Composition mo per cent H
Pyridine and			
n-heptane	95.5	74.7	70.0
n-octane	109.5	43.9	35.0
n-nonane	115.1	10.1	6.5
n-decane	zeotropic mixture		
Acetic acid and			
n-heptane	91.8	87.0	55.1
n-octane	105.8	47.0	31.8
n-nonane	113.0	31.0	17.5
n-decane	116.95	20.5	9.9

4. Discussion of results

In Fig. 5 are given the composition in weight percentages of a series of ternary positive-negative and binary azeotropes. In Fig 6, all binary and ternary saddle azeotropes examined are together graphically represented on a single diagram, the weight percentages being replaced by molar ones. It can be readily seen that the points corresponding to the compositions of the saddle azeotropes lie on a common curve $Az_1Az_2Az_3Az_4$ and that the straight lines drawn through the points representing the concentrations of binary (A, H_l) and ternary $(\frac{1}{2})Az_1$ azeotropes, cross at a common point Z' (Fig. 6).

The composition of positive-negative azeotropes changes with the boiling temperature of corresponding hydrocarbons. Certain important regularities are obvious. The concentration of acetic acid in a series of azeotropes appears as a linear increase, while the change in the concentrations of pyridine and the corresponding paraffinic hydrocarbons is shown graphically in the form of a curve similar in shape to a parabole (Fig. 7).

The boiling temperature range of hydrocarbons forming positive negative azeotropes with acetic acid-pyridine, may be approximately determined by extrapolation of the data given in Figs. 6 and 7. This range is located approximately between 90°C. and 200°C. A more detailed

analysis of experimental data, which, in view of exigencies of space, can but be touched on in this paper, shows that the compositions and boiling temperatures of mixtures represented by points lying on the

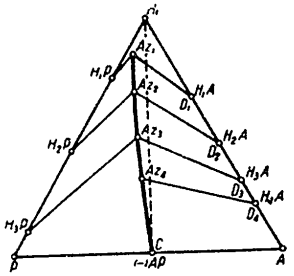

Fig. 5. A series of ternary saddle azeotropes [(−)(*A*, *P*), (+)(*H*$_I$)] formed by *A*-acetic acid, *P*-pyridine. *H*$_I$ — *n*-paraffinic hydrocarbons: (*H*$_1$*P*), (*H*$_3$*P*), (*H*$_2$*P*), (*H*$_1$*A*), (*H*$_2$*A*), (*H*$_3$*A*), (*H*$_4$*A*), [(−)(*A*, *P*)] binary azeotropes; (±)*Az*$_I$ — compositions of the saddle azeotropes in weight per cent.

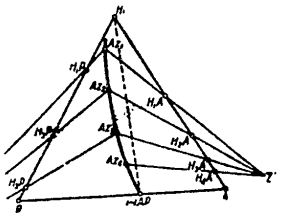

Fig. 6. A series of ternary saddle azeotropes. The compositions are expressed in mole per cent. A detailed explanation of symbols is given at Fig. 5.

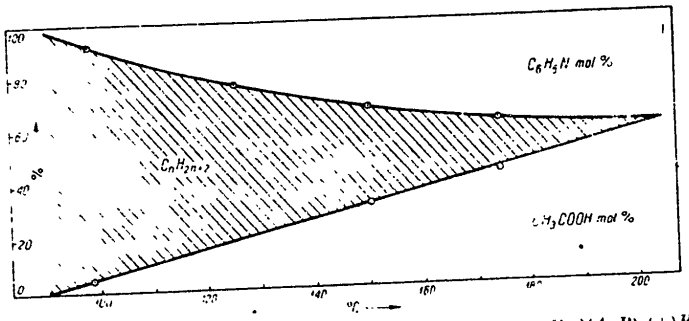

Fig. 7. Mole concentration changes in a series of saddle azeotropes [(−)(*A*, *P*), (+)*H*$_2$][(+)*H*$_I$] as a function of boiling temperature of the non-polar component hydrocarbon *H*$_I$.

top ridge line may, if the boiling temperature isobars for all of the binary systems are known, be determined with sufficient accuracy. Such a generalization may prove to be a first step towards further understanding of the phenomena under investigation. It is also possible to

calculate fairly accurately the boiling temperature depression of a ternary saddle azeotrope in comparison with the boiling temperature of a binary negative azeotrope [(−)(A,P)], if one considers the latter as one of the components and applies a correlation similar to that applied by Lecat [9], or recently by Malesiński [7] with regard to a series of binary azeotropes. For this purpose, it seems to be reasonable to use an equation in which the square root of the value of azeotropic depression is a function of the boiling temperature of the non-polar component H

5. Concluding remarks

In a series of saddle azeotropes formed by a non-polar component (hydrocarbon), a weak acid (acetic acid) and a weak base (pyridine), there appear certain regularities, which enable an interpolation of the compositions and the boiling temperatures of azeotropes formed by corresponding paraffinic hydrocarbons. It is worthy of note that the projection of the top-ridge line is slightly shifted from the main line towards the "pyridine" side of the concentration triangle. This may be explained by the fact that the azeotropic range of pyridine $Z_P(H_i)$ is smaller than that of the acetic acid $Z_A(H_i)$ in relation to a series H of corresponding hydrocarbons. This means that the boiling temperature isobars in binary systems of acetic acid and hydrocarbons are characterized by minima on the corresponding isobars lying much lower in comparison with the boiling temperatures of corresponding mixtures of pyridine and hydrocarbons. Hence, a greater convexity appears on the tridimensional surface of the boiling temperature isobars in the part adjacent to the side AH_i. This favours the shifting of the top-ridge line towards the PH_i side. Further details concerning this matter will be published elsewhere. It should be emphasized that the top-ridge line projection is always shifted from the main line towards the greater content of that azeotropic agent which has a lower azeotropic range in relation to a series H. Some exceptions seem to exist in instances in which $t_{H_i} > t_A > t_P$

I am greatly indebted to Prof. W. Świętosławski for enabling me to carry out these experiments, as well as for his valuable advice. I wish to express my thanks also to Mrs M. Zięborakowa and T. Drozdowska, W. Brzostowski and A. Turski for experimentally investigating individual ternary systems.

Summary

1. An investigation was made of a series of positive-negative (saddle) azeotropes formed by acetic and pyridine with paraffins: *n*-heptane, *n*-octane, *n*-nonane and *n*-decane.

2. A geometrical generalization was given, establishing the correlation between the compositions of the binary positive pairs of azeotropes and the saddle ternary azeotrope.

3. It was established that the shape of the tridimensional surface of the boiling temperature isobars in positive – negative systems, as well as that of the top-ridge line or its projection, depends on the values of the azeotropic ranges of the weak acid and the weak base in relation to a series of non-polar substances, e. g. hydrocarbons.

DEPARTMENT OF BASIC ORGANIC RAW MATERIALS,
PHYSICOCHEMICAL INSTITUTE, POLISH ACADEMY OF SCIENCES

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